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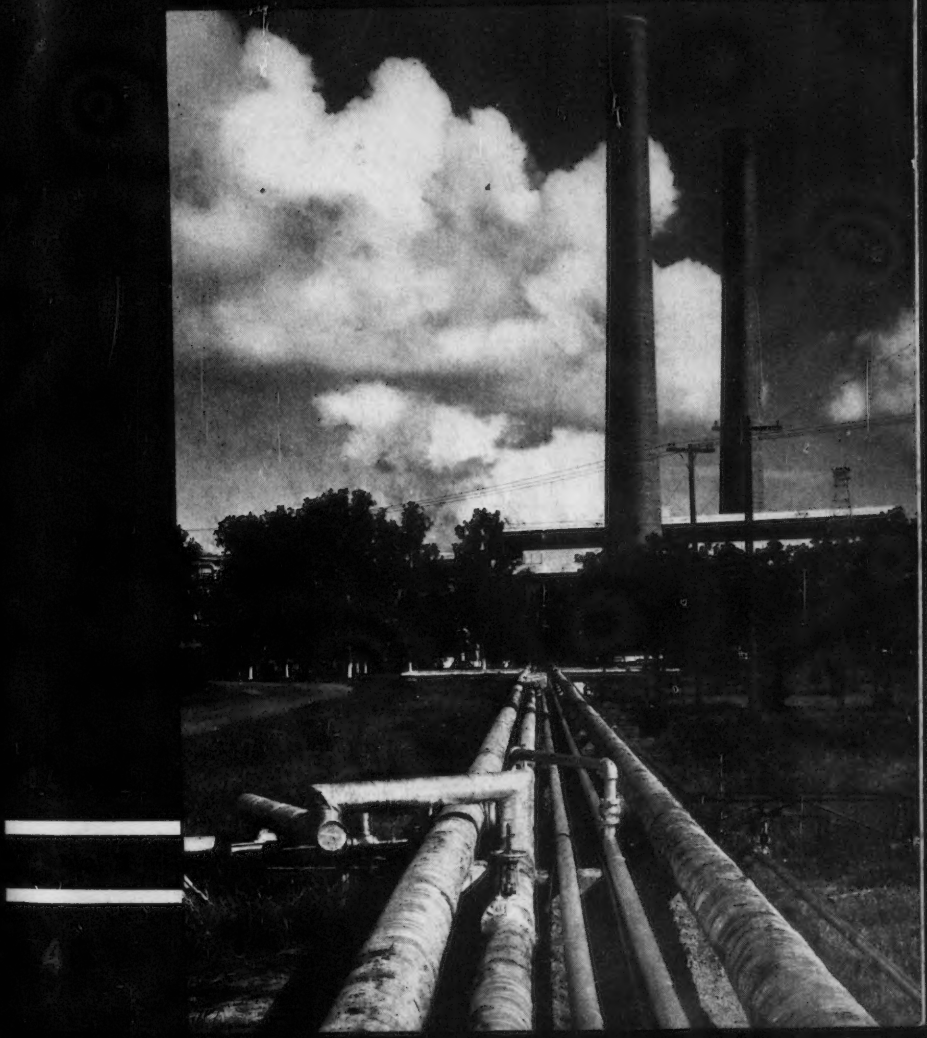

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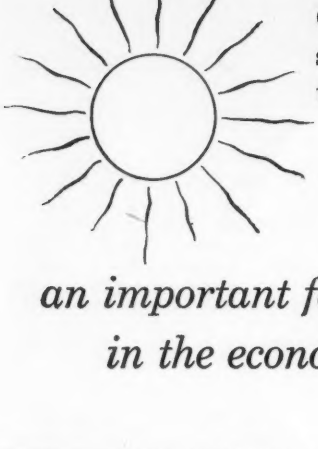

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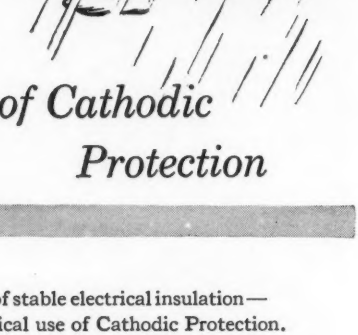

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Corrosion

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CORROSION

Research and Control

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THIS MONTH'S COVER

• *Powerhouse of the Texas Gulf Sulphur Company at Newgulf, Texas, showing hot water lines, steam, air and cold water lines to the sulphur producing area. Corrosion problems encountered in this and allied chemical plants are too many and varied to enumerate here, but corrosion control as practiced in these plants represents a major factor in maintaining high production levels at low cost. Photograph, courtesy Texas Gulf Sulphur Company.*

Slowed down to 107 years

. . . *but still going!*

Pres. Martin Van Buren

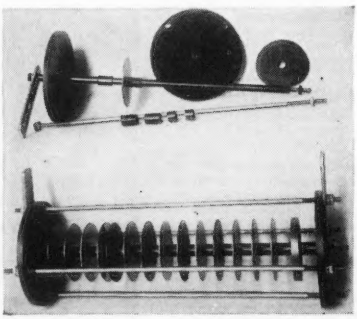
IN THE YEAR 1840, when the population of the United States was only 17,000,000 and Martin Van Buren was President, an electrical apparatus started ringing in the Clarendon Laboratory at Oxford University, and it has been ringing continuously ever since. The bells are powered by the original two Zamboni piles. These are essentially small voltaic batteries, only about 1 inch in diameter and 5 inches high. But these unusual batteries contain 2000 tiny zinc-copper elements! A Zamboni pile therefore packs a terrific electromotive force for its size. For an instant it can deliver a very high charge, said to be several thousand volts. When two piles are fastened to bells as shown in the diagram, a pith ball placed between them is thrown from side to side by alternate attraction and repulsion. Modern versions of the Zamboni pile were put to very important uses in the late war.

CORROSION SLOWED DOWN

Here, then, is an example of a corrosive reaction carefully planned to proceed at a very slow rate. This situation represents a practical requirement often faced by corrosion engineers and often solved in a similar manner, that is, by utilizing low rates of corrosion. It seems perhaps superfluous to add that if the galvanic corrosion rate of a Zamboni pile were actually zero, the apparatus would have lost its news value even while President Van Buren was still in office.

INFORMATION AVAILABLE TO ALL

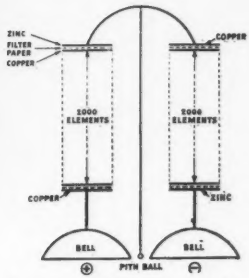
Corrosion resistance is not a fixed property. It varies greatly with media and operating conditions. To help you eliminate *or minimize* the uncertainty that often accompanies the selection of materials for a given corrosive application, The International Nickel Company offers its experience, facilities and accumulated data.



Spool-type specimen holder—a most useful device for plant testing of corrosive and galvanic effects on selected materials under controlled conditions. In practice, about 12 different materials are mounted in duplicate on the spool.

The corrosion engineering research pro-

The Clarendon Building at Oxford University, England.



A diagram of the Zamboni bell which has been ringing continuously since 1840 in the Clarendon Laboratory at Oxford University. Reproduced through the courtesy of DISCOVERY, London.

gram started by INCO about 40 years ago has helped put metal selection on a scientific footing. Laboratory studies, plant tests, atmospheric and marine tests have all contributed to an extensive fund of corrosion data to guide designers and buyers of equipment.

Throughout the years, the guiding policy of the program has been to use Nickel alloys where they belong and to best advantage. This policy has resulted in the accumulation of a classified library of more than 30,000 data sheets covering as many practical problems.

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One type of apparatus used at the Bayonne laboratory for control of motion, temperature and aeration in immersion corrosion tests.

Main research Laboratories of The International Nickel Company, at Bayonne, N. J. A separate section is devoted to corrosion research.

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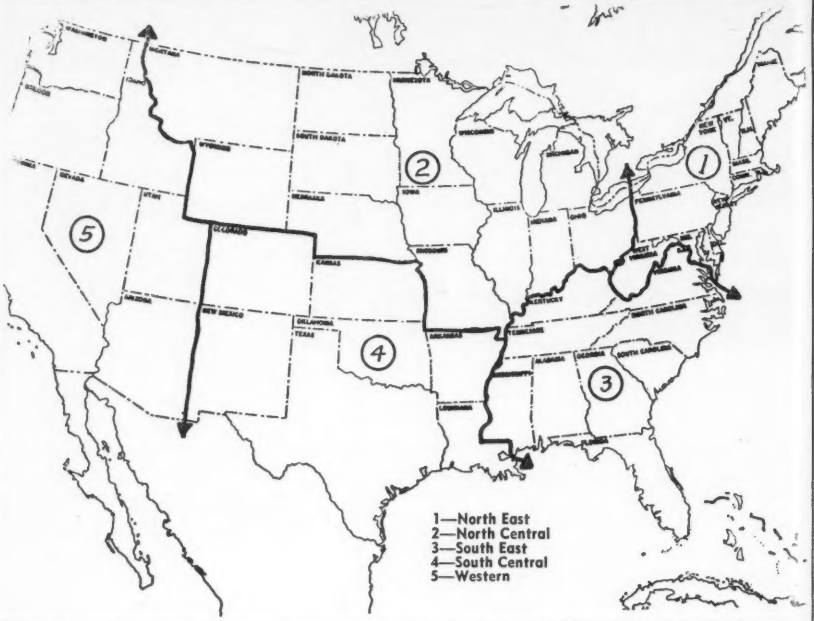

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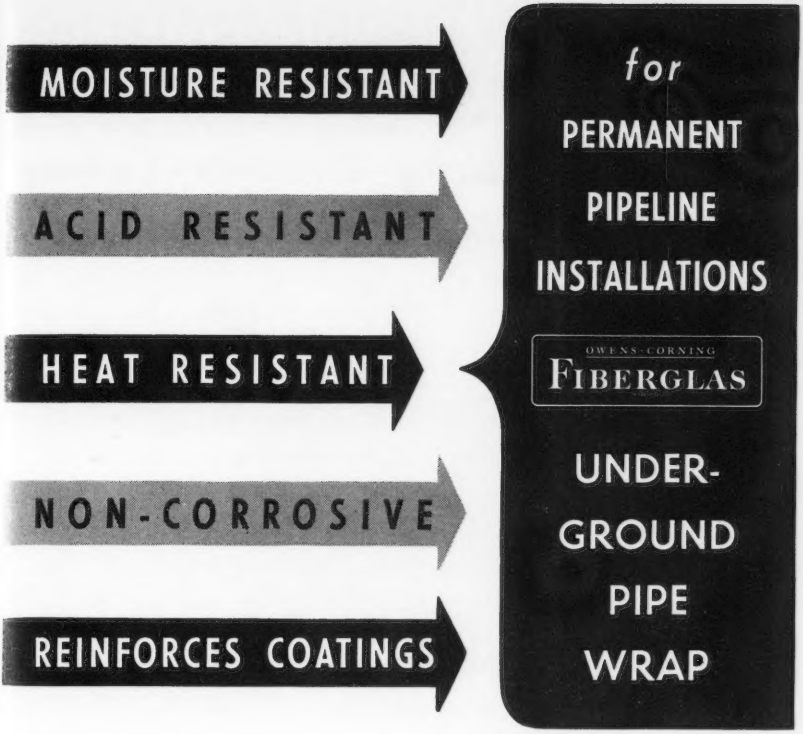

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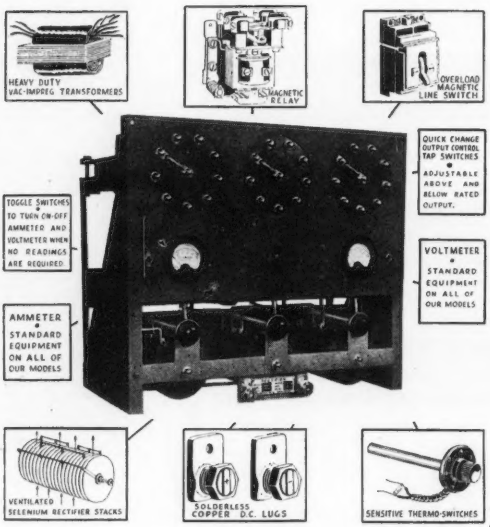
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(b) to provide a means of exchange of knowledge and ideas among those individuals actively engaged in the control of corrosion.

(c) to promote methods of control of corrosion.

(d) to promote standardization of terminology, methods, equipment and design in the development of methods of corrosion control.

(e) to foster cooperation between individaul owners of metallic structures in the solution of their joint corrosion problems.

It is an incorporated association without capital stock, chartered under the laws of Texas. Its affairs are governed by a Board of Directors, elected by the general membership. Officers are nominated by (1) the Board of Directors, or (2) a quorum of at least 25 members, and elected by the membership.

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Tests, Properties of Corrosion-Preventive Lubricants for Lead-Sheathed Cables in Underground Ducts—A Discussion*

By Howard S. Phelps and Frank Kahn***

ONE OF THE most serious problems associated with the operation of lead-sheathed cables in underground ducts is that of corrosion. In dry ducts, however, lead sheathing does not corrode because lead is substantially corrosion free in the absence of moisture. Since a permanently dry underground environment is exceptional, the equivalent of the dry condition is sought by providing a suitable protective coating which will prevent access of moisture to the sheathing.

A large number of grease-type and solid-type coatings have been proposed for this use. The grease-type coatings are applied to the cable while it is being installed and function also as pulling lubricants. The solid-type coatings are essentially factory applied (not adapted for field application) and include paints, waxes, cements, plastics, and oil-resistant synthetic rubbers.

Cable-Pulling Greases

Approximately 20 years ago it was observed at Philadelphia Electric Company, that a tacky axle grease, used sparsely as a pulling lubricant on cables in a particularly corrosive environment, effectively prevented corrosion on the areas to which is was applied, while adjacent uncoated areas were severely corroded. It was also observed that other greases then in use as pulling lubricants did not have this corrosion-preventive feature, undoubtedly because they did not permanently exclude moisture.

The marked corrosion-preventive effectiveness of the axle grease led to an investigation of available greases, including cable-pulling lubricants, to select the best one for the purpose. Although the axle grease originally used left much to be desired in certain properties, none

★ A paper presented at the Annual Meeting of NACE in Chicago, Ill., April 7-10, 1947.

* Engineer in Charge, Special Investigation and Testing Division, Philadelphia Electric Co., Philadelphia, Pa.

** Senior Technical Assistant, Testing Section, Philadelphia Electric Co., Philadelphia, Pa.

of the other greases investigated to date has been found outstandingly superior to it. However, the investigation has resulted in the development of specifications and a number of performance tests for a corrosion-preventive cable-pulling compound. It is hoped presentation of this material will stimulate petroleum engineers to develop a product having the desired characteristics.

Desirable Specifications for Corrosion-Preventive Cable-Pulling Lubricant

The properties primarily desired in a corrosion-preventive pulling lubricant for lead-sheated power cable are as follows:

(1) Good adhesion to lead sheath and resistance to flow, over a temperature range 10° F. to 165° F.
(2) Self-healing in air and under water.
(3) A good lubricant (cause no excessive pulling stresses during severe cold weather) and maintain a continuous lubricating film between cable and underlying duct wall.
(4) Insoluble in water, and shall wet the metal in preference to water.
(5) A good insulator for low voltages (of the order of several volts).
(6) It shall not gum or harden, nor cement cable to duct walls.
(7) Chemically inert so that there shall be no detrimental action on either the cable sheath or the duct.
(8) Chemically stable and shall not be affected by nor become pervious to soil waters in the range of pH 2 to 12.
(9) Have a flash-point sufficiently high to obviate fire hazard.
(10) A relatively good heat conductor.
(11) Permanently maintain the foregoing qualities.
(12) Time and effort of application shall be reasonable.

Performance Tests

Relatively simple tests for some of the foregoing properties have been developed by Philadelphia Electric Company and are set down in the form of test specifications.

1. Adhesion to Lead and Resistance to Flow

1.1 The compound shall have good adhesion to lead sheath and be resistant to flow, over a temperature range of 10° F. to 165° F. This requirement shall be determined by the ring test described below.

1.2 *Ring Test.* A specimen of the compound shall be applied in the form of a ring approximately one inch wide and one-sixteenth-inch thick to the surface of a length of cylindrical commercial lead sheathing approximately three inches in diameter. The lead surface shall be clean and unscored and the compound shall be wiped on with the fingers to assure wetting of the surface, but without excessive working of the compound. The lead cylinder shall be suspended with axis horizontal in air maintained at a constant temperature of 110° F.

1.3 Once each week the following visual observations shall be made.
A. Amount of compound which drips from the cylinder. If more than a few drops, this should be reported in terms of approximate percentage of total volume of coating.
B. Degree of thinning of compound on top and sides.
C. Occurrence of bare spots and spots covered only with a thin oil film.

2. Self-Healing in Air and Under Water

2.1 The compound shall be self-healing in air and under water. This requirement shall be determined by the following scratch tests for self-healing.

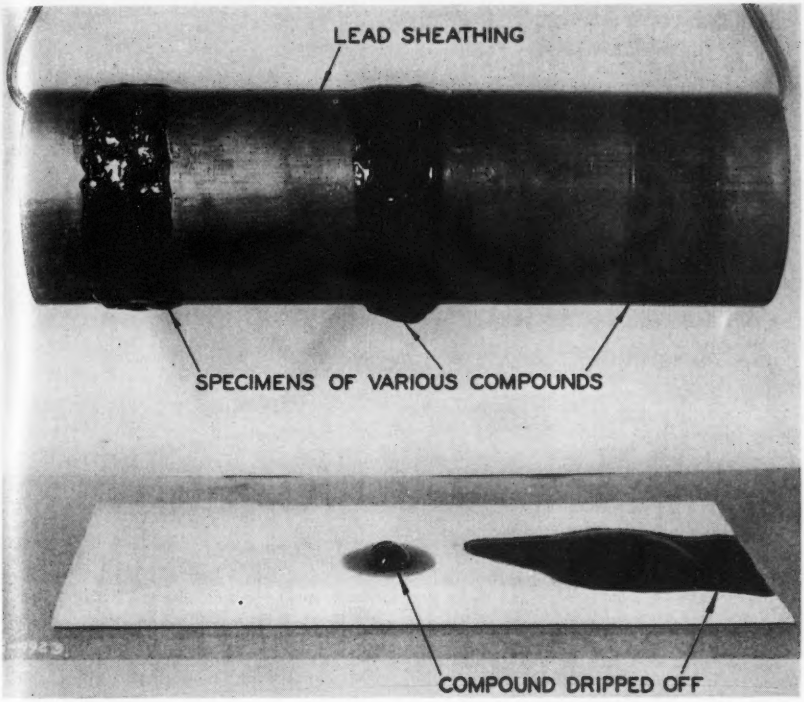

Figure 1—Length of lead sheathing on which are applied Ring Test specimens of compound undergoing tests for Adhesion to Lead Resistance to Flow, (Item 1 of Specifications).

2.2 *Preparation of Scratch.* The scratch test specimen shall comprise a small patch of compound, approximately one by two inches in area, applied on a clean plate of flattened commercial lead cable sheathing to a thickness of slightly more than one-sixteenth inch by wiping on as in Item 1.2. A scratch about 1½ inches long shall be made in this coating, using a sheet metal tool comprising a straight edge having a one-eighth-inch-long stepped projection which extends outwardly one-sixteenth inch. When held perpendicularly and moved across in firm contact with the lead surface, this tool produces a square-shouldered channel in the compound with walls one-sixteenth-inch high.

2.3 *Scratch Tests for Self-Healing in Air.* Two scratch test specimens, prepared as described in Item 2.2, shall be disposed horizontally, with the coated surface of one upward and the other downward, in air maintained at a temperature of 110° F. If desired, a single lead plate coated on both sides may be used in place of two discrete plates.

2.4 The following visual observations shall be made at least once each day for the first week and then once each week:

A. Estimated percentage of each scratch healed over with oil film.

B. Estimated percentage of each scratch healed over with main body of compound.

2.5 *Scratch Test for Self-Healing Under Water—No Voltage Applied.* This test is identical with that of Item 2.3 except that the test specimens, instead of being in air, are immersed in a solution of five percent sodium chloride in distilled water,

maintained at a temperature of 110° F.

2.6 The following observations shall be made once each week:

A. Visual estimate of percentage of each scratch healed over with oil film.

B. Visual estimate of percentage of each scratch healed over with main body of compound.

C. Proof voltage and film resistance test at 1.0 volt ac on each scratch specimen at room temperature.

The specimens shall be removed from the vessel containing the saline solution and allowed to dry and cool to room temperature. The scratch shall be faced upward and filled brimful with the saline solution.

An electrode of the same composition as the lead plate, and of contact area approximating half the plan area of the scratch, shall be suspended over the scratch and in contact with the saline solution. A suitable source of 60-cycle ac potential shall be connected to the plate and to the electrode and the voltage between them raised gradually from zero to one volt rms and held for one minute.

The leakage current shall be observed during this test. The coating shall be considered unhealed or broken down if the leakage current exceeds one milliampere. If the specimen withstands this test, the resistance, computed from the leakage current at one volt, shall be reported.

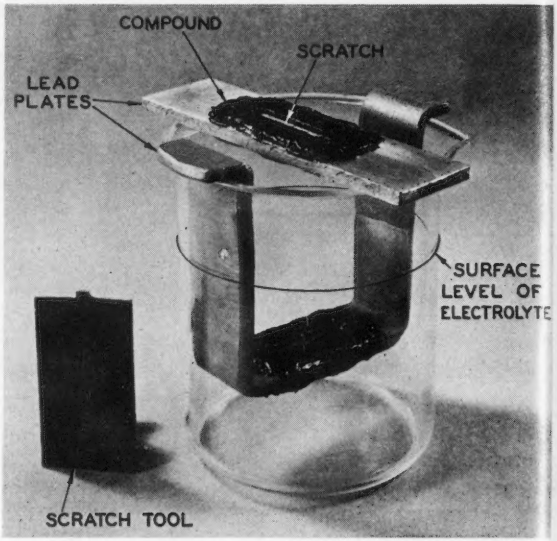

Figure 2—Set-up used in making Scratch Test for Self-Healing in air and under water without applied voltage (Items 2.3 and 2.5).

2.7 *Scratch Test for Self-Healing Under Water—At 0.75 Volt D-C.* In this test a dc voltage of 0.75 volt is maintained between two electrodes which have been coated with the compound, scratched, and immersed in five percent sodium chloride solution in a sealed cell maintained at a temperature of 110° F. The electrodes shall be plates of flattened sheathing lead completely coated with the compound to a thickness of not less than one-sixteenth inch. The scratches shall be made in the manner described in Item 2.2, but shall be one inch long, three-thirty-seconds inch wide, and one-sixteenth inch deep. The electrodes shall be suitably insulated from each other externally of the electrolyte, and the scratched surfaces shall be disposed horizontally and shall face downwardly.

2.8 The following observations shall be made at least once each week:

A. Current magnitude.

B. Visual indications of corrosion.

3. Lubricity

3.1 The compound shall have adequate lubricity to prevent excessive cable-pulling stresses even during severe cold weather. This requirement shall be determined by the lubricity tests described below.

3.2 *Lubricity Test Apparatus.* The fol-

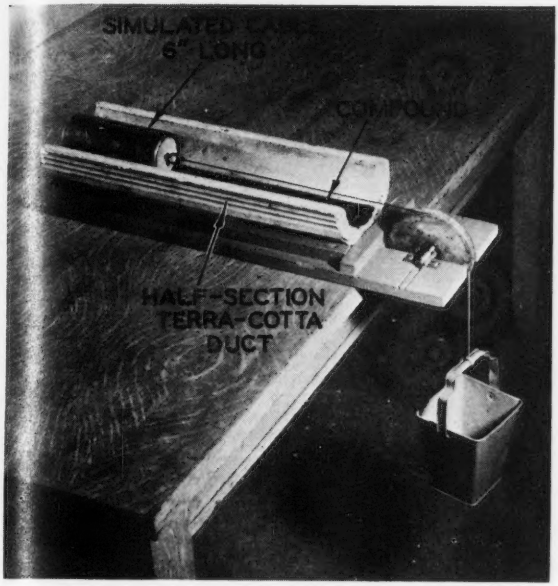

Figure 3—Apparatus used for making Lubricity Test, (Item 3.2).

lowing described apparatus is designed to measure the force required to pull a length of lead-sheathed cable, lubricated with the compound, along a duct section at a predetermined constant speed. The duct shall comprise a split 18-inch section of four-inch terra-cotta duct fixed in horizontal position. The cable shall be approximately 2¾ inches in outside diameter and six inches long and shall have a uniformly distributed weight of six pounds, which may be obtained by a simulated core. This cable shall be provided at one end with an axial pulling eye and the ends of the lead sheathing shall be rounded with a curvature of one-eighth-inch radius. A low-friction ball-bearing pulley, rotatable in a vertical plane, shall be so disposed with relation to the duct that the axis of the cable when lying in the duct is tangent to the top of the pulley groove. A cord engaging the pulley shall support a freely suspended adjustable weight and have its other end attached to the pulling eye.

3.3 *Lubricity Test.* A coating of the compound, approximately two inches wide and one-sixteenth inch thick, shall be applied to the bottoms of the duct section and the cable for their full lengths and the cable laid gently in the duct at the end farthest from the pulley. Cut-and-try determinations shall be made of the weight necessary to pull the cable at an average speed of 15 feet per minute over the length of the duct section.

The value so obtained, doubled, shall be considered the pulling force per foot of lubricated cable. This determination shall be made at temperatures of both 75° F. and 35° F.

4. Integrity of Coating

4.1 The compound shall be a good insulator and shall maintain its integrity and adherance to lead in soil water environment. This requirement shall be determined by the leakage current cell tests described below.

4.2 *Leakage Current Test Cell.* The test cell shall comprise a sealed glass jar containing an electrolyte of five percent sodium chloride in distilled water in which are suspended three one-inch-wide strip electrodes of cable sheating lead immersed in two inches, disposed parallel to each other at three-quarter-inch spacing.

Before immersion, the two outer lead-strip electrodes shall have all sharp corners rounded and smoothed and a coating of the compound, not less than one-sixteenth-inch thick, applied, covering the portion to be immersed and extending one inch above the water line. The middle electrode shall be left bare. An external electric connection shall be available for each electrode and a suitable adequate water-repellent electric insulating medium (asphalt plastic cement, for

example) shall be applied to their upper parts within the cell to minimize surface leakage.

4.3 *Cell Test.* The cell shall be maintained at a temperature of 110° F. and dc voltages of three volts shall be applied between the middle bare electrode and each of the outer coated electrodes, one outer electrode being positive and the other negative to the middle electrode.

4.4 The test shall comprise operation of two duplicate cells.

4.5 The following observations shall be made at least once each day for the first week and then once each week, on each cell:

A. Leakage currents in the lead to each coated electrode, obtained with a galvanometer of high current sensitivity.

B. Visual estimate of the amount of compound which has become detached from the electrodes.

5. *Field Experience*

5.1 The time and effort of field application of the compound shall be reasonable and it shall not possess any unsatisfactory characteristics or deficiency which impairs its performance.

5.2 *Field Test.* Provided the foregoing tests have indicated the compound should give reasonably satisfactory performance, a full scale field trial should be made by a crew familiar with application of such coatings. If possible this should be done at the two extremes of working temperatures.

5.3 The following observations should be made:

A. Difficulty of application.

B. Any adverse features including pathological and psychological factors.

Duration of Tests

Most of the foregoing tests are of a continuing character. Accordingly, the question naturally arises as to an acceptable minimum duration of the test period to produce the information desired.

As soon as the compound under consideration develops a decidedly unsatisfactory characteristic in any of the tests, the material should be rejected and all tests thereon discontinued. In the absence of marked failure under any of the tests, each should be continued until it becomes reasonably apparent that a substantially stable condition has been reached.

Figure 4—Electrode and container comprising test cell for leakage current tests at three volts dc for Integrity of Coating (Item 4).

Experience indicates that six months should be adequate for the tests for Adhesion to Lead (Item 1) and Self-Healing (Item 2). It is believed the test for Integrity of Coating (Item 4), however, should be continued for at least two years.

Little has been done in the way of developing markedly accelerated tests for any of the desired characteristics, because performance under the accelerated condition could not be related to experience in the field.

Criteria of Compliance With Specifications

Because of meagerness of results available for some of the tests, it was thought advisable to withhold for the time being all proposed criteria of compliance with the foregoing specifications. However, some gen-

eralizations can be indicated from comparative results on a number of compounds tested.

Referring to the Ring Test for Adhesion to Lead (Item 1), the results, after a month, range from a compound which showed no change, to one in which more than half the material had dropped off, leaving areas of the ring completely devoid of the compound.

In the Scratch Tests for Self-Healing (Item 2), the results range from complete self-healing to complete lack of self-healing.

In the Lubricity Test (Item 3), the results range from a pulling force of the order of two pounds per foot of cable to the order of 20 pounds per foot at 75° F., and from eight to 80 pounds per foot at 35° F. It is recommended that a compound, under this test at 35° F., should not require a pulling force in excess of 20 pounds per foot of cable.

In the three-volt, dc Cell Tests for Integrity (Item 4), leakage currents in some cells have remained at less than one microampere for over a year, while in one cell the current increased steadily to several milliamperes in a month. In this test for integrity there is little doubt that the leakage current should never continuously exceed a few microamperes.

Field Application of Compound

At Philadelphia Electric Company, the grease is applied by hand with one man applying handfuls of grease on the sheathing and another wiping or rubbing in the grease by hand. The rubbing action presumably assures that the lead is wetted by the grease despite the presence of casual dust, dirt or even moisture on the sheathing.

The compound is applied with as thick a coating as possible, filling the belled duct mouth around the cable. For approximately three-inch cable in five-inch duct it is not feasible to apply the coating to more than about one-eighth inch average thickness. Although it is believed a minimum thickness of one-sixteenth inch would be satisfactory, it is applied in excess with the prospect of achieving at least this minimum. Any excess thickness will tend somewhat to fill in thin spots or perhaps to accumulate at the underside of the cable which would not be undesirable.

Mechanical applicators which do not rub the grease on, are likely to apply patches or films of grease which do not wet or bond to the surface. Eventually these spots will probably be without protection. A bond of grease to lead presumably might be assured with such a device if the cable is thoroughly cleaned and/or wetted with the grease before it enters or is engaged by the applicator. Furthermore, unless a very thin coating will suffice, mechanical applicators for field use must solve the not inconsiderable problem of providing a reasonably concentric or uniformly thick coating.

Field use of a compound sometimes developed unsuspected difficulties. In 1933, it was decided to use a complete coating of the axle grease formerly used sparingly as a lubricant as a corrosion-preventive. Although there apparently had been no objection on the part of the field crews to applying a few handfuls of

this grease for lubricating purposes, its copious application was a disagreeable job. For some time after this program was established, the prejudice against use of this material necessitated continuous supervision of application to prevent occurrence of ungreased areas.

Another instance of the advantage of field trial occurred in the development of the Lubricity Test (Item 3). Laboratory tests had indicated a certain compound to be quite promising, particularly in having remarkably good self-healing and adhesion to lead. Its viscosity, by ASTM test, was approximately the same as the original axle grease used as a standard of comparison. A laboratory lubricity test was then devised, in which a polished steel disc was permitted to slide down an adjustable-inclined plane of plate glass lubricated with the compound. The results of this test indicated the compound and the axle grease to have roughly comparable lubricities, and that the compound under consideration merited a field trial.

In the field trial of this compound, excessive pulling stresses were developed. It was then reasoned that the inclined glass plane test was in the nature of a measure of viscosity. The present proposed Lubricity Test (Item 3) simulates actual cable-pulling practice and apparently gives results comparable with those found in the field. It is believed this test satisfactorily takes into account the internal shearing stresses developed in the compound during actual pulling.

Test Temperatures

The properties of the compounds investigated to date were considerably influenced by temperature. As the temperature was raised, these compounds softened and had increased tendency to run off. In contrast, their self-healing and lubricity characteristics were improved with increase in temperature. Although it would be desirable to know in what way the characteristics vary with temperature, this would require very extensive tests. In the interest of simplification, it was decided to test the compounds at a single temperature, frequently occurring in service, at which results obtained could be considered generally indicative of the relative merits of the various compounds.

Some cables are operated in the field with sheath temperatures as high as 165° F. Although it might be considered desirable to obtain performance characteristics for this extreme condition, the complications incident to performing the tests at such an elevated temperature did not seem warranted. To facilitate testing procedure, the temperature selected had to be one readily maintained yet well above any ambient likely to occur. Identical considerations in the testing of physical characteristics of lead sheathing had led to the adoption of 110° F. as a suitable test temperature. For the foregoing reasons the temperature of 110° F. was selected.

Conclusion

This investigation has indicated that development of a completely satisfactory corrosion-preventive cable-pulling lubricant will not be readily achieved. However, several producers are currently engaged in research on this problem and promising progress is being made.

Use of Inhibitors in Corrosion Control*

*By Norman Hackerman**

CORROSION of metal installations, such as plant equipment, liquid holders, liquid and vapor producers, etc., is so common that it is a problem of industry-wide concern. Inter-industry cooperation, in terms of investigational effort, is as great if not greater in this field than in most other common efforts. The solution of each problem is a useful contribution to the general fund of directly applicable knowledge. Its importance lies just as firmly, however, in the fact that it supplies data for use in fundamental studies. Such accumulated data, when properly digested, along with carefully reasoned and executed experimentation, supply the basis for generalization. This, in turn, becomes useful in further application to individual problems.

A procedure of this type is well exemplified in the study of corrosion inhibition. The introduction of chemicals into corrosive media, or application of chemicals to metal surfaces, for purposes of retarding or halting the dissolution of metals is widely practiced. In many cases, the practice is that of an art rather than a science. This is true despite the fact considerable literature of scientific research has been built up during the past 20 years in this field.

The intent of this article is to cite the use of a number of specific materials, to show that the effectiveness of a material as an inhibitor in one instance does not make it generally applicable, and to consider several theories of corrosion inhibition—particularly the relation of absorption to such action.

For present purposes, any substance injected into the system which interferes with the dissolution of a metal will be considered an inhibitor, regardless of the mechanism by which it operates.

Inhibition by Effect on the Corrosive Medium

In the most obvious category of corrosion inhibitors are those materials effective by virtue of their ability to remove one or more corrosive substances from the corrosive fluid. Perhaps foremost among these agents are the neutralizers which may be used to counteract acid attack. The injection of ammonia into gas condensate wells has been reported[1] successful in reducing attack by the lower fatty acids. Treatment

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with ammonia, to bring the pH to 9.5, inhibited high temperature attack of water and carbon dioxide in a boiler system[2]. The removal of dissolved oxygen from the corrosive medium, for example by the use of sulfites[3], frequently eliminates corrosion to a great degree. It has been shown[4], for example, that bearing metal is not attacked by fatty acids in the absence of oxygen or organic peroxides. The use of formaldehyde[5] in reducing sulfide corrosion in producing oil wells may be attributed to the formation of a polymer, into which the sulfide is bound. One author[6] states that a reaction occurs between the sulfides and the formaldehyde, and the product of this reaction forms a thin film on the steel. This substance is reported effective in reducing attack of hydrogen sulfide saturated brines or acid solutions on steel by as much as 80 percent. Seemingly, inhibition in the latter solution occurs mainly at lower temperatures. Finally, tin and cadmium compounds are believed to inhibit the action of citric acid on steel by removal of sulfides from the solution[7].

Inhibition by Effect on the Metal-Inorganic Chemicals

Probably the most widely used of these substances is sodium chromate (or, in some instances, sodium dichromate). An early paper[8] dealing with chromates clearly delineated the advantages and disadvantages of this inhibitor with respect to steel in water or salt solutions. A decreased efficiency at higher temperatures and in the presence of chlorides was noted. This effect has been verified by subsequent research. There is, however, ample evidence of the usefulness of chromate inhibitors in many industries. For example, the injection of chromate into refrigerating and air-conditioning units is now commonplace[9]. About 0.5 percent by weight of sodium chromate (along with some hexametaphosphate) is introduced into acid dye solutions to counteract the attack on stainless steel equipment[10].

Treatments for Cadmium, Zinc and Aluminum

It has been reported that immersion of cadmium-plated articles in a sodium dichromate-sulfuric acid bath prevents attack on the cadmium by humid atmosphere. Without this treatment it appears that cadmium plate fails more readily than zinc[11]. Chromating processes have been devised for zinc[12] and for aluminum[13], and chromate inhibition of the latter metal in phosphoric acid, well water, and other media has been shown to be effective[14].

Chromates in primer paint pigments have been in use for several years, with zinc chromate apparently the most effective. Strontium chromate (discussion to Reference 9) has been suggested in this connection and potassium barium chromate[15] was recently reported a good possibility. The last two compounds are somewhat more soluble than the zinc salt and it is probable that the readier availability of the chromate ion would enhance the inhibitory properties of the primer.

Oxygen is a component of the system in all of the examples cited above, and in most cases there was free access to the air. However, successful use of sodium chromate in protecting condensate gas wells, an

acid, anaerobic system, has been reported[16,17].

Phosphates and Silicates

Phosphates have been proposed and used in water systems[18]. These substances not only tend to inhibit corrosive attack on steel, brass, lead, zinc, and aluminum, but also function as scale removers. For small water systems, sodium silicate has been recommended as an efficient inhibiting agent[19]. Furthermore, it has been used successfully for several years in various phases of the petroleum industry[20]. The disilicate has been found to prevent the action of alkali on aluminum, concretely both for toothpaste on collapsible tubes and in hot soda ash solutions[14]. In the latter instance, high concentrations of the disilicate are needed. Sodium nitrite[21] is said to be an inhibitor for steel in aqueous solutions in which the pH is not less than six. The presence of chlorides has a deleterious effect on the efficiency of this material, as it has on all of the inhibitors mentioned in this section. The general requirement is that more of the inhibitor be added when chlorides are present. Nitrites have also been used for steel exposed to gasoline, alcohol, isopropanol, ethanol, and other organic compounds.

Other Cations Investigated

Laboratory tests have been carried out to determine whether certain cations might be useful as corrosion inhibitors. Among those investigated were zinc, manganous, chromic[22], arsenious[23], and antimonous salts[24]. The latter two have been found helpful for steel in sulfuric and hydrochloric acid, respectively, provided the hydrogen evolution type of corrosion was predominant. Practical application of arsenic, in the form of $NaAsO_2$ or As_2O_3, to inhibit steel in 65-70 percent sulfuric acid is imminent[25]. The same report noted that presence of copper ions cancelled the effect of arsenic compounds. Also, in sulfuric acid, the inhibitor showed little value with chemical lead, admiralty metal or brass, and was only partially effective for monel. None of the first three have indicated more than fair inhibiting properties with a system of steel in water. Red lead[26] and red oxide[36], which may be properly included in this group, have been used widely in base coat paints. The former seems to have definite inhibiting capacity, but there is some question as to the function of the red oxide.

Two agents usually thought of in terms of corrosive attack have been shown to act as corrosion retarders in some cases. These are oxygen[27] and water[14]. Oxygen may be placed in this category when it is present under high pressure or in alkaline solutions. The presence of a little moisture apparently reduces attack on aluminum equipment during distillation of organic chemicals like phenol, the alcohols, and the fatty acids, because corrosion of this equipment increased when the last traces of the water were removed.

Inhibition by Effect on the Metal-Organic Substances

A large number of individual organic compounds have been tested in the laboratory and in practical operation, with representatives of all classes of polar organic sub-

stances having been tried. Many of these inhibitors have been pure substances but a large portion finding industrial use are crudes. The active ingredient in these crude materials is not always clearly delineated; in fact, it seems likely from a close perusal of the available information that in many cases the inhibiting action can be attributed to impurities. Inhibitors in this group are used to a large extent for acid type attack, e.g., acid pickling of steel. They need not be limited to such uses, however, because they have given evidence of their effectiveness in water and in salt solutions as well.

Oxygen-Containing Compounds

Among oxygen-containing compounds, the ketones and carboxylic acids apparently have been the most effective. A commercial inhibitor containing a relatively small amount of a cyclic ketone markedly reduced gas condensate well corrosion in one Texas field. Commercial naphthenic acid has proved to be about 50 percent effective in corroding gas wells in several fields.

The major constituents in this mixture are probably cyclohexane carboxylic acid and cyclopentane carboxylic acid, or substitution products of these compounds. There are many more compounds in the mixture, however, and the relative amounts of the constituents vary from batch to batch. A series of patents[28] claims that a number of long chain dicarboxylic acids containing a sulfur, selenium, or tellurium atom somewhere in the chain is effective in reducing corrosion of steel by water or salt solutions. Brass is affected by rapeseed oil at 150° C., and this attack was eliminated by the introduction of 0.05 percent by weight of succinic acid[29] to the oil. The same paper reported that brass bearings were protected from groundnut or mineral oil by either oxalic acid or ethyl oxalate in the amount of 0.05 percent by weight. Aldehydes have been used only infrequently, one specific case being formaldehyde, as noted earlier.

Alcohols, in general, have not shown much evidence of inhibiting capacity. However, Evans states that inhibition by alcohols should improve with the number of hydroxyl groups on the molecule. It has been conclusively established that the chrom-glucosates[30], which are derivatives of glucose (a six carbon compound containing essentially six hydroxyl groups) are of practical value in reducing corrosion in water systems. As in the case of the phosphates mentioned previously, these materials are also scale removers.

Nitrogen-Containing Compounds

Undoubtedly the organic compounds which have been scouted most thoroughly in attempts to find corrosion inhibitors are those containing nitrogen. The aliphatic and aromatic amines have been variously reported as very effective[31], and only moderately so[32] under approximately the same conditions, i.e., for acid attack on steel. In contrast, there is complete agreement on the effectiveness of heterocyclic nitrogen compounds in acid attack on steel as well as other structural metals. Most research relating inhibition by organic materials to absorption

phenomena has been done with nitrogenous compounds.

Sulfur-Containing Compounds

Sulfur-containing compounds, frequently mentioned as likely inhibitors by analogy to nitrogen compounds, have been used in relatively few instances, probably because of the lesser availability of such materials as much as for any other reason. Several sulfur-containing compounds have been suggested, however, and a few are now on the market. Substituted thioureas were patented[33] as corrosion inhibitors about 20 years ago; and dibutylthiourea diethylthiourea are produced commercially for this purpose now. The dicarboxylic acid patent mentioned earlier specified the presence of a member of the sulfur family in the molecule. The successful use of mercaptobenzothiazole for inhibiting corrosion in products pipelines should also be noted[34].

Colloids

A number of substances of colloidal nature have been tried as inhibitors, and some have been reported as effective. Gelatine is reported to retarded the action of sulfuric acid on iron when present in about 1.25 percent by weight[35]. Natural gums and glue have been suggested, and use has been made of the latter in preventing the alkaline attack which toothpaste causes on aluminum[14]. Heavy metal soaps have been used successfully in experiments in this laboratory in essentially eliminating the reaction of steel with acetic acid under anaerobic coditions. The soaps which proved useful were manganese and iron salts of naphthenic acid, although the cobalt soap was ineffective. The effective inhibition exhibited by red lead and linseed oil has been attributed, in part at least, to the basic lead soaps which form[36]. Oil in water emulsions[37] have been used to protect steel coolers in water circulating systems. The colloidally dispersed oil is said to function by forming a thin layer on the steel, but it is also possible that the emulsifying agent provided some of the inhibiting effect.

Miscellaneous Inhibitors

There are a number of other inhibitors which are unquestionably of organic origin but which can not be categorized very easily. For example, raw beet sugar and raw cane sugar are known to inhibit corrosion of iron in water and dilute salt solution. The raw cane sugar is the less effective of the two[38]. The inhibiting properties are related to the impurities since the refined product in each case was ineffective. Another interesting material, reported very recently, is made by evaporating a solution of sodium chloride or sulfuric acid containing a linseed meal extract[39]. One percent of the resultant material is said to effectively retard the action of the mineral acids on steel.

Consideration of Factors

The phrase, ". . . alleged corrosion inhibitor, triethanolamine . . .", was used in a recent article. Such statements are indicative of the fact that there is not yet general appreciation of the idea that corrosion inhibitors are not universal in application. One might be led to believe, then, that in order to find a suitable corrosion inhibitor it would be necessary to test an inordinate number

of compounds and mixtures. However, if the system under consideration is studied from the point of view of the type of corrosion present, the corrosion products formed, and the chemistry of the system, as well as the particular metal to be protected it is possible to eliminate many substances and concentrate on a few which might be effective.

Types of Corrosion

In determining the type of corrosion it is desirable to know whether the effect is purely chemical, or whether electrochemical action is to be expected, or whether a mixture of these types may be obtained. In addition, it is necessary to know if the corrosion is of the hydrogen evolution type or if it is controlled by the rate at which oxygen can diffuse to the surface at which reaction takes place. For example, if it can establish that hydrogen gas is evolved it may then only be necessary to treat the system in such a way as to make the deposition of hydrogen more difficult. On the other hand, other types of corrosion processes can be retarded by eliminating a factor already present, rather than by using an additive. Very frequently it is found that an inhibitor is more effective for a metal when it is alone than when it is found in a polymetallic system. It is evident that in more complex systems the agent may cause an inhibiting effect on surfaces other than that chosen for protection and either provide no protection for the metal, or, worse, accelerate the corrosion on that metal.

Nature of Corrosion Products

The nature of the corrosion products may well determine the procedure to follow since a slight change in conditions, temperature for example, may be sufficient to produce solid corrosion products which will be protective enough and thus eliminate the necessity for the addition of foreign materials. As an example, in the exposure of zinc to water and to zinc chloride solutions it was found that the lowest rate of attack occurred in 0.015-0.040 M solutions.[40] It was pointed out that under these conditions the α-hydroxide forms whereas in water alone the β-hydroxide is obtained, and in more dilute solutions the oxide precipitates. The alpha form has a laminated structure and correlation is claimed between greater resistance to penetration of this solid and the lower corrosion rate. In gas condensate wells, surfaces are covered with a scale containing ferrous carbonate principally. This scale impedes access of the corrosive liquid to the basis metal and therefore reduces the rate of attack. In many wells, however, sufficient scale thickening takes place to cause cracking of the barrier and subsequent localized attack. Strange as it may seem, the use of carbon dioxide as an aid in such systems might be considered, although the solubility of the carbonate in the acid solution may obviate any advantage. Injection of chemicals to plug the relatively "porous" carbonate is a possibility. This rests on an analogy to some work done with soaps on phosphated steel surfaces.[41] This report showed that an alkaline lubricating soap was taken up *on* the phosphate coating, but an acid soap entered the pores of the layer.

Chemistry of System

By knowing the chemistry of the system is meant determining (a) whether the inhibitor might react with other materials present, (b) if the reaction product or the original form is an effective inhibitor, (c) if the reaction products are corrosive agents, and (d) if an inhibiting agent introduced into a polymetallic system for one metal is a corrosive agent for another.

Effect of Temperature

At temperatures in the region of 500° F., naphthenic acid has been found to be quite corrosive on mild steel, 18-8 stainless steel, and cast iron.[42] In this laboratory it has been demonstrated that a medium containing naphthenic acid, acetic acid, water, and hydrocarbons is quite corrosive to mild steel coupons, provided air is accessible to the system. With identical solutions but in the absence of air, naphthenic acid reduced corrosion of steel by acetic acid to a negligible amount. Naphthenic acid acted as a retarding agent in this case, since acetic acid corrodes steel to an appreciable extent in the same system with the inhibitor absent. It is probable that naphthenic acid attaches to the metal surface by chemical bonds (see below) and in aerated systems oxidation produces a ferric naphethenate which diffuses into the solution where it is hydrolyzed, thereby reproducing the acid to repeat the cycle.

Sodium Chromate

Many investigators believe that sodium chromate acts by reacting with the metal ion produced by dissolution, to give a solid mixture of oxides which forms on the surface and stifles further reaction,[43, 44] On steel, the mixture would contain Cr_2O_3, Fe_2O_3, and possibly Fe_3O_4, the oxides in general being hydrated. The presence of solid, green chromic compounds in chromate inhibited gas condensate wells is plainly evident on the tubing. The effectiveness of this inhibitor has been clearly demonstrated in at least one well.[45] Scale formed on coupons exposed to this gas stream at the well head contains chromic oxide, but the iron compounds have not yet been identified. The only information thus far obtained is that the material is magnetic. This well, originally corrosive, has been treated for about two years with consistently satisfactory results.[16] A two-month exposure of well-head coupons (from this laboratory) has shown no significant weight change, and only a very slight thickening of the scale during that period. In other wells, equally desirable results have not always been obtained, although some reduction of corrosion rate has been found in many of them. A problem peculiar to wells which show high dissolved solid contents in the produced water has been encountered, namely that of plugging. This may be due to the alkalinity conferred locally by the chromate solution at the point at which it enters the gas stream. Laboratory experiments have shown that the rate of consumption of chromate in anaerobic, acid solutions is quite high. Furthermore, on pulling the tubing of a well which had been treated with chromate, reduced chromium was found over a considerable length of the exterior surface of tubing. Ob-

viously, if the chromate ion itself is the inhibiting agent,[46] or if the reduction product is not deposited on the steel directly, no retardation will be obtained or at best, large amounts of make-up will be needed.

Examples of corrosive agents formed by reactions of the inhibitors are less familiar. The addition of arsenic salts to inhibit acid attack on steel may lead to plating arsenic metal on portions of the metal surface where, in contact with the iron, it could conceivably act as an accelerator of electrochemical attack. Such a phenomenon would occur if the system were such as to allow hydrogen depolarization to take place, since the overvoltage of hydrogen on arsenic is the reason this metal is operative as an inhibitor.

The clearest example of the difficulty of adding an inhibitor for one metal in a polymetallic system is found in the use of ammonia or strongly basic amines. In solutions of pH greater than seven, such substances will certainly act to dissolve copper and its alloys, as well as other metals which form complex metal amine ions.

Excessive Consumption of Inhibitors

The effect of excessive consumption of inhibitor in restricting corrosive attack to smaller areas (note: the overall rate of attack is not necessarily increased) of the metal surface is of paramount importance. Attention has been called to this factor many times, but usually in connection with the injection of insufficient quantities of inhibiting agent. Increased temperature, causing higher reaction rates or hydrolysis, and the presence of certain ions, notably chlorides, accentuate the losses by consumption of the inhibitor and therefore the danger of localization.

Theories of Inhibition

The most widely accepted postulate involves the formation of surface layers or films, which reduce the ease of access of the corrosive materials to the metal surface. Such scale can be formed naturally, as pointed out above, or can be induced to form. In the latter case it is maintained that compounds of the metal ions precipitate on the surface as the metal dissolves. This is believed to hold in particular for the inorganic inhibitors as a group since many of the heavy metal compounds of the oxygen-containing anions are insoluble. The presence of the solid can be demonstrated. Furthermore, it can be shown, by studies of the temperature coefficient of the corrosion reaction, that the rate is controlled by the rate of diffusion of solute to the metal. It is well not to overlook the fact that a good case can be made out for a mechanism in which the anion attaches to the metal surface without undergoing significant change in its chemical constitution. Such a possibility has been advocated by Uhlig[46] for the chromate ion.

Adsorption

The organic inhibitors have evoked a larger number of postulated mechanism, most of them based on adsorption (attachment of a particle to the solid surface) of the

molecule to the metal thereby causing retardation. Some investigators[31,47] favor the idea of adsorption at the cathodic areas and its effect as a blanketing factor; others,[33,48] its effect on hydrogen overvoltage on these areas; still others,[32,35] the increase in cell resistance due to film resistance. Some[35,47,49,50] prefer the idea of fairly complete coverage of the surface by an adsorbed film, i.e., not limited to either anodic or cathodic areas, and the subsequent effect on the accessibility to the metal atoms in the surface. The adsorption effect shows up clearly in experiments on the wetting ability of numerous substances,[51,52,53] since wetting depends to a large degree on the relative interfacial tensions of the solid and the corrosive liquid on the one hand and the same with an additive on the other.

Strength of Adsorption Bond

The strength of the adsorption bond has not been scrutinized to any extent until quite recently. A suggestion has been made that the polarizability of a molecule and its inhibiting capacity can be correlated.[54,56] The idea of chemisorption (attachment by true valence forces) merits close attention. Mayne[55] and Uhlig[46] have advocated this approach and the work in this laboratory is pointed in that direction also.

In many of the articles cited,[31,32,48,49,54] mention is made of increased effectiveness of inhibitors after a short time interval. Moreover, Ardagn and his co-workers[49] found that when an inhibitor was added to a medium which was being stirred, the retarding efficiency was less than when no agitation was used. Significantly, when the inhibitor was added to the quiescent solution and stirring was instituted after about five minutes, the inhibitor efficiency was not decreased. One characteristic of chemisorption, as contrasted to adsorption by physical forces alone, is that the process is not instantaneous, and the experiments cited tend to show that chemisorption is a factor in inhibition. This point might be countered by the possibility that the lag is due to the time required for orientation. Another significant fact lending credence to the chemisorption idea is that in many of the papers mentioned, specificity of inhibitor action is noted. Attachment to specific solid surfaces is also characteristic of chemisorption processes. Still another supporting factor is that there is some evidence, although the data are scanty, to show that appreciable difference in heats of adsorption are obtained with different substances of the types generally used as inhibitors. It is known that the energy changes in chemisorption are measurably greater than in physical adsorption.[54,56]

The work here indicates that the molecules are held to the surfaces by adsorption and that some are held by stronger bonds. For example, some of the polar organic materials adsorbed on steel powder can be desorbed almost completely by washing with solvent whereas others can be removed only to a limited extent. Adsorption of both physical and activated types appears to take place over the entire surface and

effectively prevents further reaction of the metal atoms to which the adsorbed molecules are held. The energetics of the adsorption should not be so great as to weaken the remaining lattice bonds to the atom in question, since in so doing the atom may be removed from the lattice. Variation in inhibitor activity of a homologous series is explainable on this basis. For example, the lower fatty acids react with steel whereas the longer chain acids adsorb. This is not to say that the higher ones are necessarily inhibitors since other considerations are also involved. However, a prediction might be made as to relative inhibitor quality on the basis of ionization constant of an acid or basicity of an amine, for example.

Orientation Patterns of Molecules

Orientation of the molecule with respect to the surface takes place regardless of the type of adsorption involved. In addition, however, lateral orientation or "close packing" must be considered as a factor. In other words, where the inhibitor is adsorbed by physical forces they still may be effective by retarding diffusion of the corrosive. If a lateral orientation — pseudo crystal structure—is obtained, it is reasonable to suppose that the diffusion rate is reduced to a greater extent than if the hydrocarbon "tails" are randomly arranged. This corresponds in many respects to Machu's theory.[35] An electron diffraction pattern of a carboxylic acid on a steel surface has been obtained at this laboratory, and a structure both parallel and normal to the surface is observed. Other patterns obtained here indicate only monolayer adsorption, with practically no lateral uniformity. In the latter case, field use of the material—a cyclic ketone—showed it to be very effective.

Metal Structure and Adherence

Finally, the relationship between the lattice structure of the metal, the microstructure of the metal, and firmness of adherence of the surface film must be considered, Holmberg[57] and Manual[58] point to a correlation between carbide structure of steel and corrosion resistance. *Part* of this behavior it would seem could be ascribed to the effect of structure of the metal on film adherence. The effect of the subphase on the properties of physically adsorbed films was found by Jura and Harkins[59] to be marked in the case of normal propyl alcohol adsorbed on barium sulfate, anatase, and quartz, respectively. In the first case, a monolayer was formed, but in the other two, polymolecular layers obtained. The point to be made here is that the organic materials, which form "soft" crystals, are more apt to conform to the structure of the metal than is an inorganic scale and they may therefore be useful in plugging cracks or in forming a complete, pliable surface film.

Acknowledgment

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Discussion

*By M. G. Fontana**

Dr. Hackerman mentioned that one of the electron diffraction photographs showed a physically adsorbed film. In our work at Ohio State on passivation of stainless steel, we found that exposure to vacuum destroyed passivity, indicating the presence of physically adsorbed gases. According to the physical chemists, physically adsorbed gases can be removed readily by vacuum treatment. The electron diffraction camera used at the University of Texas doubtless operates under vacuum, which may remove physically adsorbed films.

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Discussion

*By Hugh J. McDonald**

Dr. Hackerman has presented a nicely summarized account of corrosion inhibitor action but his cataloging and correlating of inhibitors is still bound by the old illogical classification into organic and inorganic inhibitors and several assorted groups that do not seem to fit into any definite classification. It is much more helpful to classify inhibitors according to the fundamental chemical reactions responsible for their effectiveness. On this basis, inhibi-

* Corrosion Research Laboratory, Illinois Institute of Technology, Chicago, Ill.
** R. D. Misch and H. J. McDonald, Evaluation of Corrosion Inhibitors, Wire and Wire Products (in press).

tors may be divided into four great classes,** as follows:

1. Proton Acceptors:

This group includes all those inhibitors which pick up a proton or hydrogen ion in solution and drift to the cathodic area. It includes most organic inhibitors useful in acid media, especially in pickling operations, such as pyridine, quinoline, urea and thiourea, aliphatic and aromatic substituted amines, etc. In general, this group of inhibitors will be effective because of their action at cathodic areas.

2. Electron Acceptors:

This group will include all substances that act as inhibitors because of their ability to pick up electrons. They will be effective because of their action at anodic areas, and will include besides regular anodic inhibitors those materials commonly known as passivators. In the group may be listed chromates, concentrated nitric acid, nitrites, organic peroxides, etc., and they will be most effective in inhibiting reactions which are under anodic control, as for example, the stress corrosion cracking of mild steel. Even oxygen itself, when it reacts as a passivating agent, may be included in this group.

3. Overvoltage Modifiers:

This group is made up of all those materials which owe their effectiveness principally to the changes they bring about in overvoltage characteristics at the anode and cathode areas. It will include materials such as antimony and arsenic salts, which are effective in inhibiting corrosion of iron under acidic conditions, due to the displacement of small amounts of the antimony or arsenic by the iron. The antimony and arsenic, having a high hydrogen overvoltage, will cause the reaction to shift to effective cathodic control. In this group may also be included corrosion accelerators, such as small concentrations of platinum salts which by displacement present areas of lower hydrogen overvoltage and increase corrosion of iron and other similar metals when present in an acidic environment. The group also includes so-called "depolarizers,"—materials such as nitrates—which, due to their action in speeding up the combination of liberated atomic hydrogen to molecular hydrogen or conversion of liberated hydrogen to water, cause a lowering of the hydrogen overvoltage at these areas and a consequent increase in the corrosion rate.

4. Barriers:

Materials such as glue, agar, molasses, yeast, flour, etc., although they do act in part to increase anodic or cathodic polarization, or both, apparently owe most of their usefulness as inhibitors to their direct effect on the viscosity of the solution. This change in viscosity is especially important at the interface between metal and solution and it is at interfacial areas that foreign addition agents will tend ot collect. Most of the rate-determining phenomena in reactions involving the dissolution of metals, including corrosion, generally occur in a thin layer of the liquid, only a few microns in thickness, adjacent to the metal surface.

Discussion

*By J. T. Waber**

There are two types of inhibitors, anodic and cathodic. This latter type are "proton acceptors" while the former may be divided into those which form films or barriers and those which are "electron acceptors." This scheme of classification provides, in itself, an improved way of looking at the mode of action of the several categories.

By far the most commonly available type is cathodic. Hence, it will receive the attention in the ensuing description. It has been noted that certain organic compounds such as p-nitraniline and benzoquinone *accelerate* the corrosion attack. For a better understanding of the electrode processes it would be advisable to include these accelerators into the basic program of study.

Cathodic Inhibitors

The principal reaction which occurs at the cathode is the reduction of a hydrogen or hydronium ion. It is only natural to assume that the function of the inhibitor is to retard the overall corrosion reaction by inhibiting the already slow cathodic reaction.

Several properties of typical inhibitors have been noted which seem to have a bearing on their mode of action. They are usually basic, surface-active (i.e., mild detergents) bulky molecules, rubber vulcanization accelerators, easily adsorbed on metals and have high dipole moments.

After consideration of the various mechanisms the following seems most probable; that the inhibitors raise the overvoltage on the cathode by being adsorbed at the same active centers as the hydrogen as in the depolarization reaction. These compounds are "proton acceptors" as classified above and hence give rise to a more basic solution by the reduction of the hydrogen ion concentration. The positively charged (or acid) ion has a high dipole moment and therefore would be expected to concentrate at the metal-liquid interface. It will be preferentially concentrated at the cathode due to the electrostatic field applied by the galvanic couple. For these two reasons the concentration of the inhibitor ion (InH^+) will be many fold higher near the cathode than in the bulk of the solution. This favors the adsorption on the cathode surface. Diffusion of the inhibitor from the bulk of the solution is less likely to control the rate.

Since the inhibitor ion involves a proton it is reasonable to assume that it is adsorbed at the same active (or reaction) centers as the hydronium ion. This reduction in the active centers available for depolarization increases the overvoltage or retards the overall corrosion reaction.

The concept of poly atomic layers of adsorbed chemicals is important to the understanding of the electrochemical depolarization reaction. The cathodic surface is almost saturated with adsorbed and discharged protons. A second layer forms which

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consists of hydrated protons. The electrostatic field of the galvanic couple and of the hydronium ions distorts the electronic shell of the first layer of hydrogen *atoms* (discharged protons). This electron from the hydrogen atom results is partial bonding between the proton of the hydronium ion and the H atom. Then the proton, hydrogen atom and the electron from the metal unite to form H_2 molecules. The electrochemical reaction then depends on the electronic work function of the cathode and on the polarizability of hydrogen atoms.

The action of the cathodic inhibitors can now be discussed after this review of the overvoltage phenomena. These compounds react with a solvated proton. This proton forms a covalent bond with the unshared 2p electronic orbitals of both the nitrogen and the oxygen atoms and the 3p electronic orbitals of the sulfur atoms within the inhibitor molecule. This is the meaning of the statement that the inhibitors are "proton acceptors."

The positive inhibitor ions (InH^+) are preferentially concentrated at the cathode surface and hence it is logical to assume that they are adsorbed, by means of this bonded proton, at the same active centers as are the protons involved in the cathode reaction. Even if the inhibitor molecules were small there would be a reduction in the number of active centers, and a consequent reduction of the corrosion rate. But the effective inhibitors are all bulky molecules. The unattached ends offer steric hindrance to approach of the hydronium ions. This reduces the rate of discharge of protons and the adsorption of the hydrogen atoms even at low current densities. But these large adsorbed inhibitor ions sterically hinder also the catalytic combination of hydrogen atoms. Therefore, the second or electrochemical depolarization reaction becomes the more important. Their effectiveness is not diminished because the number of active centers available for discharge of the proton is greatly reduced, the hydronium ions are prevented from approaching the cathode for discharge and subsequent reaction with a second hydronium ion to form hydrogen gas. The further analysis of the problem will proceed by the Brunauer treatment of adsorption on partly covered surfaces.

Author's Reply

In response to Mr. Fontana's comment, we found that any one of three effects were obtained in the electron diffraction experiments described in the paper. First, some materials were found to evaporate from the metal surface when the diffraction camera was evacuated. This was shown by the fact that patterns obtained in these instances persisted for only a short period of time—just a few seconds. In general, these materials were among the most volatile studied. A second group of substances gave persistent patterns as long as the coupons remained in the camera and the patterns were lost only after a solvent

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washing treatment. The third group gave persistent patterns not only under the vacuum conditions but also after thorough washing. The last two groups, therefore, are not subject to the "vacuum effect." It is evident that this is due in part at least to the non-volatility of the substances involved.

The method of classifying inhibitors on the basis of mechanism as suggested by Mr. McDonald, and as contained in Mr. Waber's comments, has considerable merit. It does not follow, however, that the grouping previously used, and followed in this paper, is not of use to the corrosion engineer. The latter must choose inhibitors not only with respect to effectiveness but also to compatability with the system and to contamination possibilities. It is worthwhile noting that the inhibitors included in the first and fourth groups by Mr. McDonald are organic materials while those in the second and third are predominantly inorganic substances.

A second and more fundamental difference of opinion lies in the fact that the processes described by both Mr. Waber and Mr. McDonald are believed by the author to be consequences of the inhibition and not the cause of it. It is our opinion that the inhibition is due largely to either or both of the following: (1) the introduction of a slow diffusion step due either to adsorbed material or adherent corrosion product, (2) decrease in chemical reactivity of the most active portions of the metal surface by virtue of the more complete saturation of the residual valency forces at these points by chemisorbed inhibitor. Two recent papers which are of considerable interest with respect to adsorption of polar, organic substances: Bigelow, Pickett, and Zisman, J. Colloid Sci. **1**, 513 (1946); Brockway and Karle ibid **2**, 277 (1947).

Corrosion Problems in Communication And Radio Equipment Design*

*By L. P. Morris**

WE MIGHT classify corrosion problems in communication and radio equipment design as follows:

1) General classification of corrosion problems: cathodic (or most noble) protected end of the galvanic series to the anodic (or least noble) corroded end of the galvanic electrochemical activity series of metals, the presence of moisture, the presence of electrical potentials, results of insufficient cleaning, etc.

2) Hardware and metal parts considerations, protective finishes, dissimilar metals, moving parts.

3) Small electrical circuit component problems.

4) Large electrical circuit components, heavy AC iron components, structural parts.

5) General control devices.

6) Common platings, applicable to radio and electronic items.

7) Special items, meters, test connectors, cables, antennas, non-metallic corrosion, etc.

High humidity, moisture absorption, moisture adsorption, breathing of moisture-laden air, condensation of moisture in the air, and the presence of electric potentials are probably the greatest causes of the corrosion problems associated with metallic and non-metallic objects used in the communications and radio electronic equipment field.

Galvanic corrosion is always associated with the generation of an electric potential and the more corroded metal is referred to as anodic, or the least noble: and the metal less corroded is cathodic, or more noble. In an ordinary galvanic battery cell, zinc is the more corroded and is less noble, while the copper is more noble and less corroded of the materials making up the electric couple. Metals far apart in the galvanic activity series, for example, silver and zinc, should not be placed in close contact.

In addition to metallic corrosion problems, there are the non-metallic corrosions, more generally associated with fungus growths, which can cause radio and electronic

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* Galvin Manufacturing Co., Chicago, Ill.

equipment to become inoperative within a very short time, such as after intermittent use for one day. Moisture and fungi corrosion have caused failure of 50 to 75 percent of untreated ground radio and electronic equipment within a month after installation at many places in the world.

Preventive Measures

The general answer to these corrosion problems is, of course, to prevent the entrance of moisture, the use of fungicides for protection, and continued retreatment against fungus growths, the electrical insulation of certain parts to prevent the formation of electric couple potentials, and protective coatings to prevent the corrosive oxidation of both metallic and non-metallic surfaces.

It is of primary importance that the general protective measures be applied to the smallest of detailed components after the most careful cleaning and dehydration procedures have been followed.

Without sufficient protection, almost all component parts of radio and electronic equipment may become inoperative because of corrosion. In the case of metal parts, galvanic action may cause the corroding of parts that should be movable with respect to one another, corrosion of one part may cause physical structural failure of components, surfaces may become etched because of the settling of organic dusts and fungus growths thereon, and electrical short circuits may be affected by crystal growths between metallic parts, such as cadmium "fingers" or "whiskers" between the plates of vairable air condensers.

Fibre washers, supports, terminals strips and insulators may swell causing misalignment of parts, resulting in binding of supported parts, electrical leakage paths and electrical flashovers. Laminated plastic terminal strips and boards, coil forms, switch parts, connectors, etc., may be so destroyed by fungus corrosion that their insulating properties are lost, resulting in flash-over or severe reduction in electrical resistance and equipment failure. Cellulose derivative components, woods, housings, dielectrics, leather goods, cotton, linen, and paper products may be destroyed by moisture and fungi. Many insulating and impregnating waxes may support corrosion, or be slightly acid, resulting in failures of component parts.

Almost every component part of radio electronic equipment may become inoperative after short lengths of time when subjected to periodic exposure of changes in temperature and changes in humidity unless adequately treated for corrosion resistance. Ceramic insulators may become defective unless glazed, silicone treated, or otherwise moisture and fungus proofed. Severe and rigid cleaning requirements must be met before component parts are moisture proofed or fungicided for corrosion prevention.

Galvanic Corrosion

In the case of hardware and metal parts, contact area effects are important in that the general extent of galvanic corrosion is a function of the ratio of the area of the more noble metal divided by the area of the less noble metal. As an example, if one square inch of steel is galvani-

cally coupled to 100 square inches of copper the resulting corrosion will be 100 times greater than when coupled to one square inch of copper. The exposed area of the most noble, cathodic metal should be kept smaller; as for example, it is better to use a copper rivet in a steel plate rather than a steel rivet in a copper plate.

Navy Specification (Spot Welding)

In certain cases of spot welded or soldered hardware items protective electroplating should be appled before welding or soldering. To quote Navy Specification RE-13A554, "Spot welded, or soldered items, or parts fabricated from sheet iron or steel, such as audio or power transformer cases, shall be plated, once before and once after the spot welding or soldering operation; except, where soldering forms a final assembly operation, such as sealing a transformer. For these exceptions the completed assemblies shall be furnished with a suitable and acceptable finish, in accordance with applicable finish requirements of these specifications. Similar parts, which fabrication requires forming and flame welding operations, shall be plated after completion of all such forming and/or flame welding * * * Pressure contacts between metals or alloys, dissimilar insofar as corrosive action is concerned, shall be avoided wherever feasible, except for such parts as are designed for rotation." Again, in an aircraft radio laboratory specification is set down: "Spot welding of fixed members, cans, etc., is preferable to riveting owing to possibility of corrosion under rivets in tropical regions."

In the use of aluminum alloys it is quite important to pick alloys within the range of corrosion resistance properties unless special methods of protective finishing are used. If dissimilar metals are required it may be possible to electrically insulate the items or plastic coat the joints to increase the resistance in the couple circuit. When using coating insulation it is necessary to apply the insulation to both of the metals involved if the insulation is to be effective. The use of brazed joints, where the brazing alloy is more noble than the least noble of the metals being joined, is preferred over joining materials well apart in the galvanic series by threaded connections. Threaded connections between metals widely separated in the galvanic series will quickly deteriorate. Table I shows a number of metals in their correct position

Table I

Positions in Galvanic Electrochemical Series of Certain Metals

GALVANIC SERIES:
Corroded End (anodic, or least noble)
Magnesium
Magnesium alloys
Zinc
Aluminum 2 S
Cadmium
Aluminum 17 ST
Steel or Iron
Cast Iron
Chromium-iron (active)
Ni-Resist
18-8 Stainless (active)
18-8-3 Stainless (active)
Lead-tin solders
Lead
Tin
Nickel (active)
Inconel (active)
Brasses
Copper
Bronzes
Copper-nickel alloys
Monel
Silver solder
Nickel (passive)
Inconel (passive)
Chromium-iron (passive)
18-8 Stainless (passive)
18-8-3 Stainless (passive)
Silver
Graphite
Gold
Platinum
Protected End (cathodic, or most noble)

and grouping in the galvanic electrochemical series. Note that cadmium and steel are relatively near one another in the series, but that cadmium and copper are further apart. Those metals grouped together are considered near each other in the series. If the conductivity of the electrical couple circuit is maintained, low corrosion will be minimized.

Use of Zinc Coatings

Zinc coatings are primarily used for protection when the object is not used in contact with metals too far towards the cathodic or most noble end of the galvanic series. Passivation of iron surfaces by immersion in certain acids, potassium chromate, chromic acid, weak pickling solution, etc., and surface treatments such as parkerizing and bonderizing give slight surface protection but generally serve as good bases for points as protective coatings.

When electroplating for corrosion protection of chassis or structural brackets it is important to make the mechanical design compatable with the physical requirements of the draining of plating fluids, washing, etc. The shape should also permit good current distribution in the plating electrolytics into the inside corners of fabricated items. Metal corner formings, brackets, whether spot welded or riveted, should be folded so as to give good "throw" of the electrolytic protective deposits without special plating anodes or racks. It is quite common to find the inside corner plating thickness on rather conventional appearing radio and electronic equipment chassis, to be only one-tenth of that on the outside surfaces. These inside corners are most generally subject to moisture and corrosion effects. This phase of the shape factor in mechanical design is much more severe for certain types of electroplatings that do not "throw" or build up well in the plating process.

Many small electrical circuit components suffer the greatest failure due to corrosion and require the most detailed preventive measures.

Small transformers using very fine copper wires with dc polarizing potentials between the windings, and between the windings and cores are particularly vulnerable to the effects of corrosion, because copper and steel are rather widely separated in the galvanic series and also because interlayer insulations may not be chemically neutral. Such transformers should be hermetically sealed with ceramic or glass to metal fusion seals or by thorough vacuum impregnating with the highest quality moisture resistant impregnating materials. Impregnating materials are generally subject to wide variations in expansion and contraction due to heating and cooling of the parts, and as a result minute cracks may develop, permitting the breathing of moisture.

Most All Parts Affected

Small fixed and variable capacitors are particularly subject to the effects of moisture and corrosion. Wire wound resistors, adjustable resistors, fixed composition resistors, variable composition resistors, rectifiers, switches, vacuum tube sockets, cables, cable connector assemblies, and a multitude of other small insulated components of the electronic equip-

Table II

MOISTURE PROTECTION TREATMENTS FOR RADIO PARTS

Name of Component Part	TREATMENT OF PART					REMARKS
	Drying Time	Oven T°C	Impregnating Substance	Bath Time	T°C	
Special High Voltage High Impedance Coils			Ceresin	1 Hour	140°	When cool dip in Superior Compound*
Coils: (With paper insulations)	16—24 Hours	†75°—85°	WE Superior Compound	Dip	150°—175°	*
Coils: (With Bakelite or Fiber Insulation)	16—24 Hours	†100°—120°	WE Superior Compound	Dip	150°—175°	*
Transformers Audio (paper Insulation)	16—24 Hours	†75°—85°	WE Superior Compound	Dip	150°—175°	Dip winding out of case, seal off air bubbles, then pot in case*
Transformers, High Voltage Power Type	16—24 Hours	†100°—120°	WE Superior Compound	Dip	150°—175°	Dip winding out of case, seal off air bubbles, then pot in case*
Resistors: Wire Wound, Ceramic Type, Cement Coated			Rust Ban 327	30 Minutes	140°	Heat until bubbles cease. As resistors cool, dip in Rust Ban until excess remains. Wipe off excess when cool
Resistors: IRC WW4 Type	16—24 Hours	†105°	WE Superior Compound	Dip	150°—175°	Scrape Superior Compound off one ceramic end and mark value*
Resistors: Bakelite molded high resistance	16—24 Hours	65°—75°	WE Superior Compound	Dip	140°	Seal bubbles when cool and identify*
Condensers: Molded Mica (New) $R>10^9$ ohms			Ceresin		110°	Condensers are placed in ceresin after heater is removed and left until cool (<70°C)
Condensers: Molded Mica (Old) $R<10^9$ ohms			Ceresin	3 Hours	140°—150°	Check for leakage when *cool*, Repeat treatment if necessary
Condensers: Paper Tubular (New) $R>10^9$ ohms			WE Superior Compound	Dip	150°	Make sure wax covers each end—seal*
Condensers: Paper Tubular (Old) $R<10^9$ ohms First Operation			Ceresin	1 Hour	140°	Tie wire leads against tube before heating to prevent leads breaking from foil. Check for leakage when cool
Second Operation			WE Superior Compound	Dip	140°	See that wax completely fills space at each end*
Condensers: (Sealed in Cans) (for $R>10^9$ ohms)	5–10 Minutes	†100°—120°	WE Superior Compound	Dip Terminals	150°	*
Switches and Jacks: for High Voltage of High Impedance Circuits	12 Hours	†100°—120°	WE Superior Compound	Dip insulation	150°	Dip to cover insulation* *and seal air bubbles**
Wiring	**Use Flamenol for the High Impedance Circuits**					

* Seal off air bubbles, when cool, by applying tip of hot soldering iron.
† Where no oven is available heat in ceresin from one to three hours.

ment are particularly subject to moisture and corrosion effects.

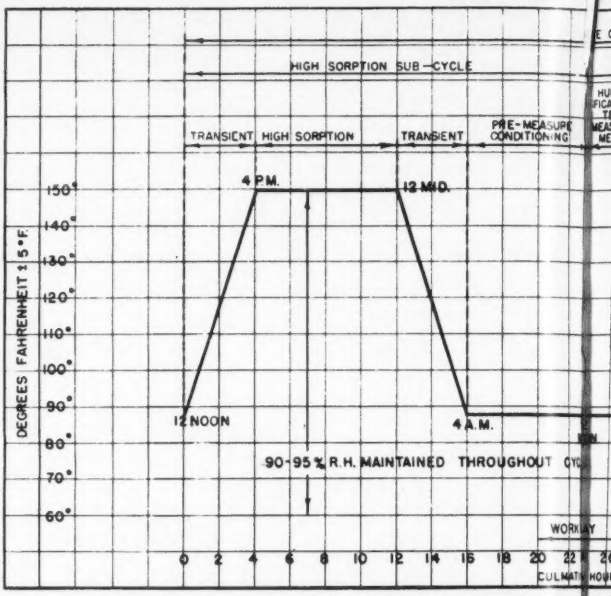
Electrolytic corrosion accounts for a large percentage of open circuit transformer windings, chokes, relays, various types of resistors, and similar equipment. These failures are caused by moisture entering small strain cracks in the impregnating material, as the result of wide temperature and aging variations. Molded mica condensers and tubular condensers are particularly subject to the effects of moisture and fungi if they are not vacuum impregnated with cerese, or other equivalent refined or natural waxes. In some cases it becomes necessary to give items an application of heat for several hours before pulling off the

moisture with a vacuum treatment.

The failures in wires, cables and cable connectors are extremely high unless great care is used in selecting the finest wire coverings for the cables and stainless steel or equivalent contacts, well insulated, in the connectors. The treatment of connectors with heat cycling followed by any of various of the silicones for moisture proofing has been quite effective.

It is extremely important to use acid-free soldering fluxes, to prevent equipment failure by reason of corrosion near soldered joints. It is extremely important that resin-core solder be used and that cleaning fluxes never be used around the soldering iron or the soldering pot because the faintest traces of carry-over will produce later detrimental corrosion. In cases where the nature of some item of an assembly has required the use of acid cleaning or soldering it is very important that strict cleaning procedures be followed before final assembly parts are put together. Many of the so-called non-corrosive soldering fluxes have been found to become acid due to heat of soldering or long time oxidation, resulting in later corrosion in the vicinity of the operation. Long experience in many factories indicates that no fluxes except carefully checked resins should be permitted in a factory building this type of equipment.

FIGURE 1—EQUI



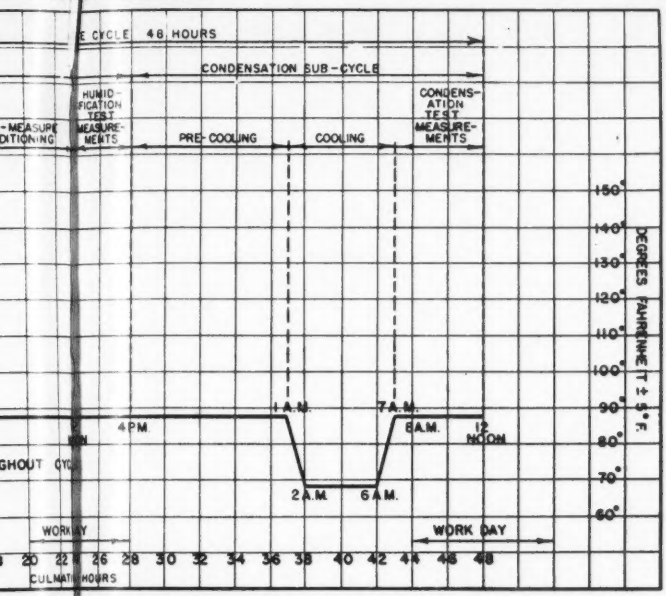
Moisture resistance test cycle was based on size of equipme to l sorbed surface moisture, breathing, corrosion of mechanical and ectr daily variations of temperature within a tropical rainforest.

To increase the rate of adsorption of moisture, 149° F. was d in to a practical period. This temperature is not considered unre ably at equilibrium by typical insulating materials is not affected b mpe

Cycle shown is not for components. Cycle for testing *individu* omp cycling may vary with the specific component under test; there inf from the Commanding Officer, Signal Corps Ground Signal Age, B

It is quite important that radio and electronic equipment operated from battery power supplies, be completely sealed off from battery compartments in order to prevent corrosion due to battery fumes or carry-over. This is especially important where components may be wound with No. 40 or smaller copper wire. Table II shows a table of radio parts moisture protection treatments, indicating the type of treatment and the materials applicable to different

1—EQUI ENT TEST CYCLE



of equipme to be tested, effect of moisture penetration, condensation, adhanical and electrical parts, temperature ranges under a tropical sun, and nforest.

49° F. was d in order to decrease the time required for making type tests dered unreasably severe, as the *amount* of moisture which will be adsorbed affected by temperature of exposure.

ng *individual* components is more severe than the above equipment cycle. This test; there information relative to component cycling may be obtained

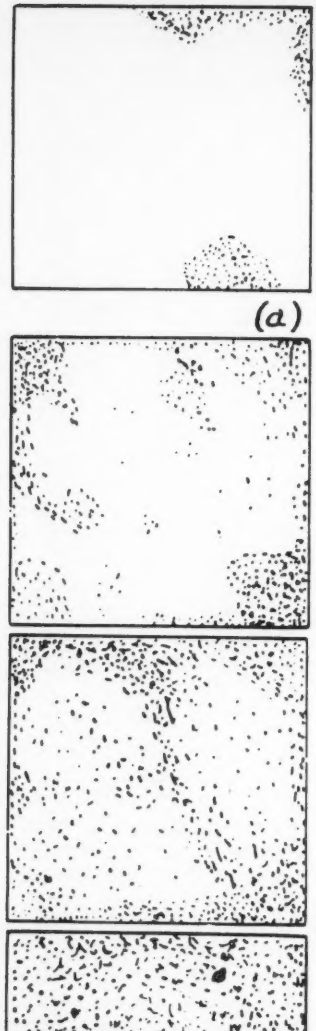
l Signal Agy, Bradley Beach, N. J.

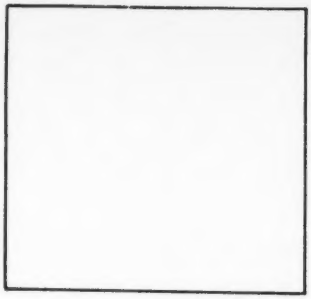
component parts. These treatments are especially important where components may be used in regions of high humidity and sudden and wide temperature variations. The table indicates the use of several different plating and sealing compounds which have excellent properties. Since this treatment chart was made up, several new compounds and treatments have been developed. One special treatment, Styraseal, developed during the war, by Utah Radio Products Co., gave striking moisture and insulation properties and was naturally fungus resistant. Notes are given on degassing or dehydrating procedures as indicated on the chart.

Large electrical circuit components such as heavy ac iron core transformers and chokes are, in general, not so adversely affected by corrosion as are smaller component parts, and the general manufacturing processes and procedures suffice for these general radio requirements. The iron or steel laminations used in magnetic circuits in general need not be plated or given special protective finishes. For larger radio component parts, one of the best general platings for prevention of corrosion is cadmium.

In general, for both large and small equipment items the conventional moisture and salt spray chamber tests are applicable. A conventional equipment test cycle, as used by Signal Corps, U. S. Army, is shown in Figure. 1

In a case of electronic and radio control devices, the comments concerning small electrical circuit components apply and in addition more complete testing should be required under more severe conditions of temperature, humidity, saline atmosphere, and tropical chamber fungus tests. Quite often the shape factor and close fit tolerance parts should be made of stainless steel rather than to take the irregular and wide





LEGEND

Type of Growth	Lab. Symbol	Mildew Resistance
No Growth	0	Good
Traces of Growth	1	Fair
Spots of Good Growth	2	Poor
Good Coverage Good Growth	3	Very Poor
Complete Coverage Abundant Growth	4	

QUALITATIVE EVALUATION OF MILDEW GROWTH

FIGURE 2

tolerances resulting from the application of corrosion preventive electraplating. Meters and measuring equipment very often should be hermetically sealed to prevent undesirable effects of corrosion at points of very small mechanical clearance.

Acids in Lubricants

In some cases, liberation of volatile acids in lubricating greases may cause corrosion, while greases in general should be neutral or slightly alkaline. Some may be found to contain 0.1 to 0.2 percent fatty acids, with chlorides present, due to oxidization. The water soluble acids, formic, acetic, propionic, etc., can be corrosive in the presence of moisture. If copper or brass parts are present certain greases may form copper soaps, which in turn actually catalyze the oxidation of the oils and change their color to green. As a test for this type of corrosion in special equipment, a polished copper strip may be partly submerged in the oil or grease for a day or so at 175 to 200° F. At the surface of the grease where the air and humidity contact the junction of copper and the surface of the grease, a copper green discoloration will result, showing oxidation and liberation of acids. A black or dark discoloration is permissible if there are no green stains. Special test equipments often have large uncovered lubricated areas for moisture protection.

Some of the more common protective metallic platings applicable to radio and electronic items are shown in Table III, with the thickness of the plating and the type of plating correlated with the amount of protection and end use required. It is to be particularly noted that the use of paint or plating on a surface does not void any applicable requirement for prior cleaning or plating. The surface cleaning prior to plating and painting is of extreme importance. It is important to watch and mask all contact surfaces where paint or plastic coating are used for surface protection surrounding desired electrical contact areas. Aluminum alloys, when used within their range of corrosion resisting properties, generally do not require protective finishes unless used in contact with metals far from them in the galvanic activity series.

Fungus Corrosion

Chief among the special items of consideration among corrosion problems in radio and electronic equipment is the subject of fungus corrosion of both metallic and non-metallic items. These types of corrosion probably cause far more failures than the strictly galvanic couple corrosions. Treatments for the prevention of this type of failure are generally termed "tropicalization treatments" and consist of the use of fungicides in combination with moisture resistant waxes, varnishes and impregnations. Special attention should be given to non-metallic corrosions where wiring and cabling materials come into contact with metal parts of the equipment.

In the use of fungicides great care must be exercised to use materials that do not gradually decompose at the operating temperatures involved. There have been many cases of gradual decomposition of the fungicides used to the extent that the

Table III

Common Metallic Platings Protective on Radio and Electronic Equipment

TYPE (ELECTROPLATED)	Protection	Thickness in Inches (Min.)	Salt Spray (Hours)	REMARKS
Cadmium	Mild Exposure	0.0002	50	On Steel
Cadmium	Severe Exposure	0.0005	100	Meets an Specs
Cadmium	Very Severe	0.001	200+	Req'd only for Unusual Conditions
Zinc	Mild	0.0002	35	Not to be Painted or Soldered
Zinc	Severe	0.0005	100	Can be Painted
Zinc (Bright)	Very Severe	0.0007 to 0.0009	150	
ZN (Ox Black)	Mild	0.0002	35	0.0002" Deposit before Oxidizing
Silver		0.00012 to 0.00018		Low Electrical Resistance
Silver		0.0003		Low Electrical Resistance. Can be Soldered
Nickel	Severe	0.0014	48	On Steel
Nickel	Severe	0.0003		On Brass
Black Ni.	Severe	ZN or CD before Ni.	50	Rust Resistant Black
White Ni.		0.0012	50	On Brass
Flash Copper	None	0.00008		Undercoat before Nickel
Copper	Mild	0.0002		
Anodized on Aluminum	Severe			Excellent for Salt Spray Electrolytic Means
Black Anodize	Severe			Durable Black Finish

CHEMICAL FINISHES NOT ELECTROPLATED

Bonderite—Treatment for Zinc to Improve Paint Adhesion
Lithoform—Used on Hot Galvanizing to Improve Paint Adhesion
Bonderizing—On Steel before Painting
Parkerize—On Steel before Painting
Cronak—On Zinc for Additional Protection
Sherardize—Zinc Iron Alloy Coating by Cementation

products of the decomposition would lower circuit resistances sufficiently to cause equipment failure. In other cases, the products of decomposition under the proper conditions would be metallic and cause direct electrical shorts or breakdowns.

Certain protective oils are often destroyed by bacteria, resulting in corrosion because of the loss of the oils and to the presence of dead and growing fungi, especially if in a fine dust or fungus laden atmosphere.

Fungus growth checks may be made by accelerated mildew inspection methods. Small specimens of culture medium samples may be inoculated with spore suspensions by spraying or dipping and transferred to clean, glass-covered glass petri dishes and set aside for incubation under specified conditions, with control samples, for a couple of weeks. After sufficient incubation, the units are rated good, fair, poor, or very poor, somewhat as indicated on Figure 2, "Qualitative Evaluation of Mildew Growth." Other fungus growth checks may be made by soil burial method for six weeks or so in a soil rich in microorganisms of the proper type kept humid by sprinkling twice daily. Temperatures are maintained at about 90° F. These

types of corrosion are many and most varied and the preventive treatments are numerous and varied.

The technique of driving out all moisture from radio and electronic components is as important as the technique and type of material used to moisture proof the components following the dehydration.

The primary problems of the design of communication and electronic equipment from a corrosion standpoint are: to obtain sufficient surface and internal moisture protection of dehydrated components, to use contacting metal parts as close together as possible in the electrochemical galvanic series, to make certain that all internal component materials are chemically neutral and not contaminated in the manufacturing processes, and to determine that all metal protective coatings are compatable with the base materials and associated platings.

Gas Utility Underground Pipe Corrosion Mitigation Practices*

*By A. H. Cramer**

THE NEED and importance of adequate underground pipe protection and periodic examination is now recognized by practically all progressive gas utilities. A gas utility's underground structures, the mains and services, represent a large percentage of its total capital investment. The large investment must be guarded in a manner that will provide maximum economy and safety when first costs, maintenance expense, and life expectancy are considered.

The purpose of this article is to present a general discussion of underground pipe protection practices that are followed by a gas distributing company in urban and suburban areas.

Prior to 1926 our company's major distribution system consisted of either cast-iron or wrought-iron pipe. The cast-iron mains were laid with lead filled bell and spigot joints. The wrought-iron mains and services were connected with either flanges or couplings. In the middle twenties the use of lead for cast-iron joints was discontinued and cement substituted. After 1930, mechanical joints only were used in cast-iron pipe installations. Over the years there was a gradual change from wrought iron to steel in such systems.

The company became conscious of electrolysis problems about 1905, when it was necessary to retain a firm of corrosion engineers for a survey of the congested areas where several cases of main deterioration had taken place. In those days the rails of the street railway system were not well bonded and stray currents ran rampant; in fact, one of the large wrought-iron mains was equipped with special couplings and acted as a substation return for a number of years. Electrical measurements at the time showed the main was carrying 3000 amperes of current. The company became concerned about the current entering the cast-iron systems, thereby causing a heating up and melting of the lead in the joints, which would result in a loss of the system.

Due to the condition of the rails and the lack of cooperation on the part of the street railway systems at

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* Michigan Consolidated Gas Company, Detroit, Mich.

Figure 1—General view of coating and wrapping yard.

that time, it was necessary to bond to other structures or to electrically drain them to the railway negative returns so that potential differences could be equalized and stray current difficulties minimized. The bonds and drains consisted of heavy stranded copper wire which were connected to the gas mains.

Actually the corrosion history of the gas company underground system at that time was not bad. The reasons for this were: (1) Because of the thickness of the cast-iron pipe used, its useful life was very long; in fact, some mains that had been installed 50 to 75 years showed very little corrosion. In stray current areas, however, there were examples where the life of the cast-iron pipe did not reach ten years, and (2) The use of high resistance lead and cement joints tended to electrically isolate each section of pipe and stray currents did not travel.

Today, pipeline corrosion in the area due to stray current electrolysis is practically negligible. This condition is attributed to a great extent to the efforts of the local "Committee on Electrolysis" and the splendid cooperation of the street railway system during the past 20 to 25 years.

The Committee on Electrolysis is composed of responsible representatives from all of the utilities and municipal departments in the area, plus some private concerns which have pipeline or cable systems in the area.

Whenever a stray current electrolysis condition is found by any of the utilities on its system, joint surveys are made and corrective measures cooperatively taken.

About 1926 a high pressure steel suburban system was installed by the gas utility. This steel line was not protected against corrosion in any way; and ten years after it was installed the corrosion was so ex-

Figure 2—Removing small diameter pipe from coating and wrapping machine, and placing in yard stock.

tensive in several sections that replacement of pipe was necessary. The pipe used for replacement was field coated with tar base products. The field coating did not hold up satisfactorily, therefore the company began purchasing mill coated and wrapped steel pipe.

It was about this time that natural gas was introduced to the area and a number of extensions were made in the gas distribution system. Steel pipe was used for the majority of these extensions.

As the use of steel pipe increased, the need for protection from corrosion became apparent, and in 1938 a coating and wrapping machine was obtained by the company. This machine was used to coat and wrap small diameter pipe. The work done by this machine on company property proved very satisfactory, but desired flexibility of operation was not obtainable. As a result, in 1939 the company designed and built coating and wrapping devices suitable for protecting all sizes of steel pipe.

At the present time at a centralized location there is an efficient coating and wrapping installation (See Figures 1, 2, 3). Here all of the steel pipe used in the district, regardless of size, is thoroughly pro-

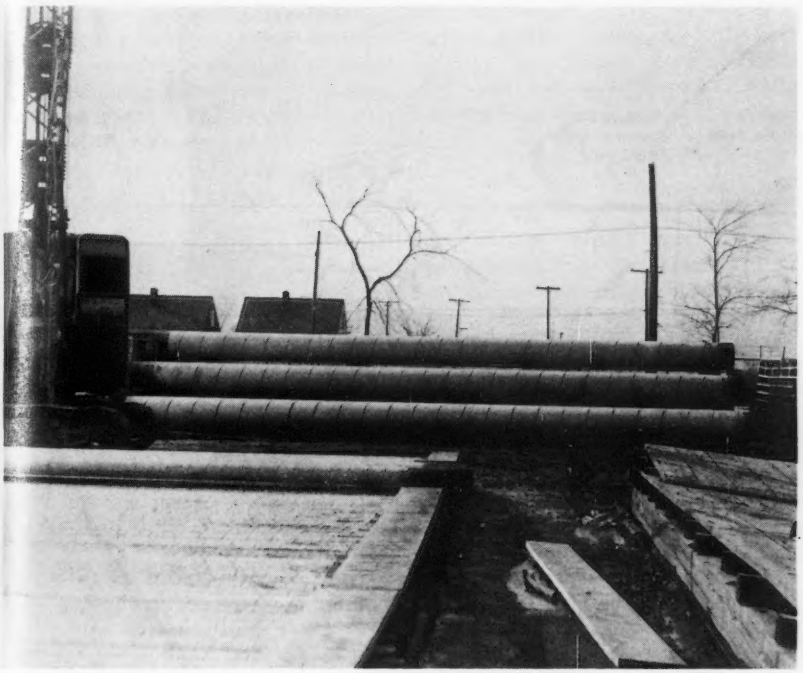

Figure 3—Large diameter coated and wrapped pipe.

tected by coating and wrapping before installation.

The coating and wrapping process consists of:

(1) Flood coating the pipe surface with a hot wax base coating.

(2) Wrapping with a dielectric wrapper which consists of a layer of asbestos, a layer of cellulose acetate, and this combination strengthened with a backing of tobacco cloth.

(3) A second hot wax coating is applied over this wrapper as a sealcoat.

(4) A wrapping of kraft paper is placed over the sealcoat to facilitate the handling of the pipe and give visual evidence of mechanical damage.

The coating and wrapping operations are under close supervision. The fact that a good job is being accomplished is evidenced by the results, which will become apparent later in this paper.

Beginning in 1940, all major high pressure distribution lines were installed using coated and wrapped standard weight steel pipe. The wall thickness of the steel pipe used is approximately 0.25 inch compared to the wall thickness of 0.73 inch of cast-iron pipe. In other words, the steel pipe has about one-third the thickness of cast-iron pipe.

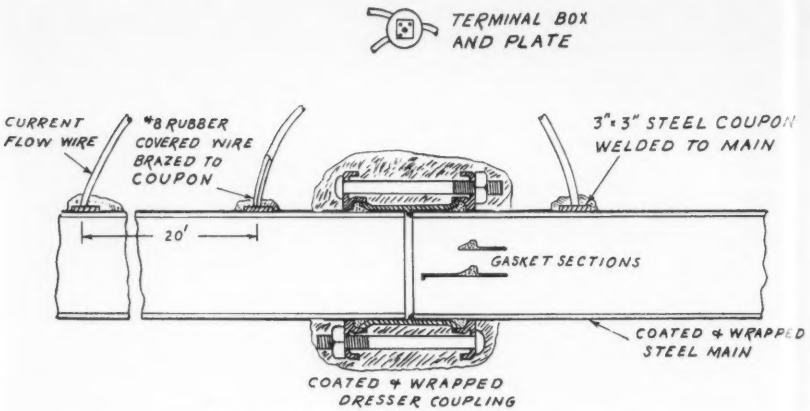
TERMINAL BOX AND PLATE
CURRENT FLOW WIRE
#8 RUBBER COVERED WIRE BRAZED TO COUPON
3"x 3" STEEL COUPON WELDED TO MAIN
20'
GASKET SECTIONS
COATED & WRAPPED STEEL MAIN
COATED & WRAPPED DRESSER COUPLING

Figure 4—Test lead connections on coated and wrapped pipe.

It was evident from the beginning that the coated and wrapped mains should be insulated from the unprotected part of the distribution system; otherwise the pipe would continue to carry any electrical current that may be picked up and transmitted by the unprotected structures.

Separation of the protected and unprotected parts of the major system is accomplished by the use of insulating couplings. Saran nipples installed with compression couplings are used to separate the major lines from small lateral lines. Coated and wrapped services are separated from the house piping with formica bushings, and coated and wrapped services to large industrial plants are separated from plant piping with insulating flanges at the meter or pressure regulator stations.

The first major coated and wrapped steel line in the system, a 22-inch main about seven miles long, is a good example for discussion of the use of insulating couplings and also the kinds of surveys or tests that are made on this type of installation.

Approximately 100 insulating couplings were used in the line. The line is frequently located only a few feet from street railway tracks or other utility structures. The insulating couplings were used: (1) wherever a tie-in was made to another part of the system; (2) wherever the line crossed under street railway or railroad tracks; (3) at spaced intervals of approximately 400 feet in straight uninterrupted runs.

On other lines in less congested areas the insulating couplings are spaced about 2000 feet apart. The insulating couplings serve to break up the continuity of flow of stray currents which may get on the line and confine any potential damage to one section because each section is electrically isolated from the other.

Thirty-three test stations were installed at approximately equally spaced intervals along the seven miles of line being used as an ex-

ample, and always at insulating coupling locations. At these stations one or more No. 8 thoroughly insulated solid rubber conductor copper wires are brazed to the mains. The free ends of the wires are located in roadway boxes or vaults so they are readily accessible for test purposes. On other lines the stations are placed at predetermined strategic locations. (See Figure 4.)

Once each year a routine electrolysis survey is made on the major distribution lines. These routine surveys provide the following information:

1. *Pipe-to-soil potential:*

During the war years, this measurement was made using a 20,000 ohms per volt voltmeter and an iron ground rod. If the pipe potential was higher than the ground potential, indication was given that stray current electrolysis could occur under the proper conditions. These conditions are high free current flow, poor coating resistance, and nearness of some medium with a lower potential. This year's survey will be conducted using a 200,000 ohms per volt voltmeter and a copper sulfate electrode.

2. *Pipe-to-soil resistance:*

This test was made using an L. & N. test set with a Wheatstone Bridge and an iron ground rod. In this test the resistance of the coating is checked. The measurements are not accurate because of the effect of stray currents on the Bridge, but are comparative. A Megger instrument will be used to take these measurements this year. The electrical resistance of the coating is the determining factor in the data, although the results will vary slightly due to soil conditions; a dry sand soil will offer a greater resistance than moist clay.

3. *Efficiency of insulating couplings:*

To check the efficiency of the insulating coupling, potential difference and resistance measurements are taken across the coupling. As long as there is a potential difference and a resistance across the couplings, it is known that they are functioning as insulators.

4. *Presence of current on coated and wrapped mains:*

This is checked by using a Wheelco potentiometer, which is a zero current potential measuring device which uses no curent from the source. The test leads used are spaced 20 feet apart on a continuous section of main. If there is an indi-

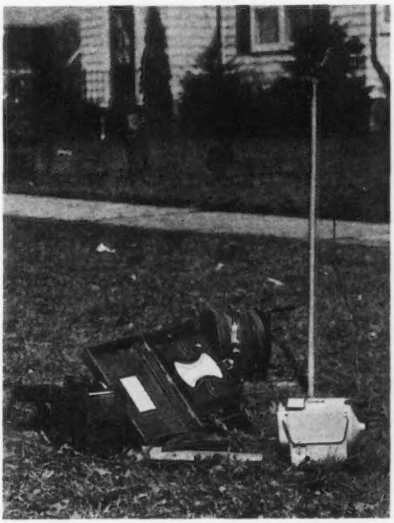

Figure 5—Instruments used for electrolysis testing.

cation of current flow, it means that stray currents are present and that breaks exist in the coating on this section of pipe, and if the current can leave the main pitting will result. (See Figure 5.)

So far, there has been only one indication of current flow on the protected system, indicating that a good job of insulation has been accomplished.

About 1940, a project was begun that called for the building of an electrical apparatus that would detect faults in the protective coatings of an installed and buried pipe.

Considerable research had been done with this type of equipment by J. M. Pearson. In an article entitled "Electrical Examination of Coatings on Buried Pipe Lines," dated January 31, 1941, Mr. Pearson presented the results of this research.

Using Mr. Pearson's suggestions as a basis, a Fault Locator was assembled and tried in the field. As is usual with first models, this one had some "bugs" in it. It was successful, however, in that it indicated possibilities in the method of checking the coating on the buried pipe.

Figure 6—Pearson Fault Locator, showing lead man and operator with receiving equipment.

In 1943, most of the "bugs" had been eliminated from the apparatus and the equipment was developed to such a point that reliable results were obtained. During the past three years a few refinements have been incorporated into the apparatus. The indicating meter and the line locating coil were eliminated. A different kind of shoe cleat was designed to give more comfortable walking conditions and to minimize weed noises.

The apparatus (See Figure 6) now consists of the following equipment: (1) A

Figure 7—Application of Locator, showing copper wire exploratory brush connected to cleat.

hummer, which propagates a 1000 cycle ac current signal in the pipeline; (2) Cleats and lead wires through which the signal is picked up from the ground; (3) An amplifier and ear phones with which the changes in signal are heard.

Current impressed on the main can leave in only two ways: (1) As leakage current through the porous coating and wrapping on the pipe itself; this results in a continuous low pitch background signal; (2) Through failures in the coating; when this occurs, voltage peaks are produced in the ground above these locations, and a very sharp rise in pitch of the background signal is observed through the amplifier.

Since 1943 approximately 300 miles of protected pipe of all sizes have been checked with the apparatus, 200 miles of which were in urban areas. The remaining 100 miles consisted of pipelines which were surveyed for other utilities interested in the apparatus.

The number of coating faults found on the 300 miles of line checked totaled 577. The breakdown of these faults is as follows:

Lines in the urban area only	400
Other locations	177
Total	577

Two hundred seventy or approximately 68 percent of the 400 fault locations in urban areas were ex-

Table I

Type of Fault	No.	Percent of Total
Accidental Coating Faults on Pre-wrapped Pipe	106	39.2
Couplings	91	33.7
Drips	23	8.5
Welds	14	5.2
Services	13	4.8
Lugs	9	3.3
Gates	8	3.0
Bonds	2	0.8
Laps	1	0.4
No Fault Found	3	1.1
	270	100.0

posed for inspection. The results are tabulated in Table I.

Coincidently 120, or again approximately 68 percent of the 177 fault locations found in the other districts, were also exposed for inspection. The results are tabulated in Table II.

Before analyzing the types of faults found, it would be well to discuss the procedure under which these electrical examinations are made.

All of the coated and wrapped pipe in the urban area, except short, small diameter services, is installed by contractors. All of the coated and wrapped pipe installed by contractors is checked first with a spark tester before backfilling operations and then with the Pearson Fault Locator immediately after installation. Any coating faults found must be repaired by the contractor before the job is accepted as being completed. This procedure immediately locates any faults that result from poor inspection or mechanical damage.

The distribution lines in the urban area consist of welded and coupled joints. The number of couplings used is a function of the weight of the pipe and the conditions along the route. For example: four lengths of 22 inch diameter pipe are usually welded together before being lowered into the trench, to be coupled to other sections; 10 or more lengths of 8 inch pipe are welded together before being lowered into the trench. In the congested parts of the city it is often necessary to use several couplings to clear some obstruction.

Several of the coated and wrapped lines were installed between 1940 and 1942 so that it was not possible to make a preliminary examination of these lines because the Fault Locator had not been completed.

After a fault has been exposed it is inspected to determine the cause of the condition, repaired, backfilled, and then rechecked with the Fault Locator.

At the locations where there is no apparent or visible fault, the pipe is tested with a copper wire brush which is connected by a lead wire to the cleats of the Fault Locator operator. With this brush it is possible to pick up faults in the coating underneath undamaged wrapper. (See Figure 8.)

Several miles of old unprotected steel pipe were reconditioned and then manually coated and wrapped. This pipe was initially uncovered by using a trenching machine with reverse buckets. The remainder of the earth was removed manually from the sides and bottom of the pipe. The pipe had to remain in service and the laterals and services pre-

Table II

Type of Fault	Number	Percent of Total
Accidental Coating Faults	96	80
Bonds—Lap	9	7.5
No Fault Found	15	12.5
	120	100.0

vented raising the pipe any appreciable distance.

The pipe was first cleaned by a portable descaling machine consisting of cutters and wire brushes which revolve around the pipe and loosen the mud and scale.

All major pits in the pipe are then filled by welding. The pipe is then coated and wrapped as follows:

(1) Apply a fluid wax primer to thoroughly wet the pipe with wax.
(2) Hand rub a cold semi-fluid wax base coating on the pipe.
(3) Wrap with a dielectric wrapper.
(4) Hot flood coat over the wrapper with a solid wax base coating to secure a good sealcoat. This final coat is "rugged" on.

Only one fault has been found on the manually reconditioned lines in the last two years with the Fault Locator.

An analysis of the faults found in the urban area revealed that 106 or 39.2 percent were in the coating of the prewrapped pipe. These faults are due to poor or inadequate inspection on the part of the contractor. These faults were found to be caused by: (1) Skid marks; (2) Bruises due to stones or sharp objects in trench before installation, or in backfill; (3) Somebody walking on the pipe; (4) Pipe coating bruised while attempting to go under other utilities' pipe; (5) Pipe coating bruised by other utilities crossing over or under the pipe; (6) Shovel marks.

Couplings Constituted One-Third of Faults

Couplings constituted 33.7 percent of the total faults exposed. These couplings were found to be inadequately coated. Bolt heads and parts of the rings were found exposed. It was necessary to inaugurate a new method for the protection of couplings. This method, although costly, is now producing the desired results, namely, very few faults.

Other Locations of Faults

The remaining 27.1 percent of the exposed faults were due to:

(1) Drips—In some cases the drip stocks were found unprotected, or the length of stock above the ground was found to be in contact with the roadbox in which it was encased.
(2) Welds—By reason of carelessness and poor inspection several welds were not protected. The contractor began backfilling before an adequate inspection could be made.
(3) Services—The service tees were found unprotected and the location on the pipe where the tee was welded was not recoated.
(4) Lugs—These lugs were welded to the main to hold caps during pressure test. They were not removed and were found to be unprotected.
(5) Gates—The gates, like the couplings, were found to be inadequately protected.
(6) Bonds—At two locations the coating was found to be poorly bonded to the pipe. This condition was probably due to coating the pipe while damp.
(7) Laps—In only one location was a poor lap found.
(8) At three locations no apparent fault could be found.

The faults found on the lines outside of the urban area consisted of

80 percent accidental coating faults. They were caused in a manner similar to those reported under accidental coating faults in the urban area. In addition, several more causes were found; these were:

(1) Bulldozer operation — Backfilling operations followed the lowering of the pipe into the ditch too closely and the coating was broken by the bulldozer blade.

(2) Swamp clamps were found that had pressed through the protective coating.

Poor bonds and laps constituted 7.5 percent of the faults. This was especially true on a line which was reconditioned and then coated and wrapped by a machine which travelled on the pipe itself. The condition was caused usually by uneven tension on the wrapper and was prevalent where the grade of the line changed either uphill or downhill.

No faults were found at 12.5 percent of the exposed locations. The figure is quite high when compared with the 1.1 percent in the urban areas. These locations were exposed and examined by persons other than the operators of the equipment. It is evident that a thorough examination, including an exploratory inspection with a spark tester, was not made.

Conclusions

The three years' experience with the Pearson Fault Locator has resulted in the following conclusions:

(1) It is a worthwhile and necessary adjunct to the other instruments used in pipe corrosion prevention work. It does not replace the conventional type of holiday detector because the proper time to repair coating faults is before the installation of the protected pipe.

(2) An electrical examination of the coating in addition to electrolysis surveys gives a very accurate check of the protected lines.

(3) It has resulted in improved coating technique.

(4) It has improved reconditioning practices because it has made the men more alert to the work they are doing.

(5) The cost of operation of the Pearson Fault Locator will vary depending upon conditions encountered. In open country on a well coated pipeline, it is possible for two men to check as high as 12 miles of pipe a day.

It is hoped that in the very near future additional refinements will be incorporated in the apparatus so that protected pipe under concrete or hard surfaces can be checked, and ac hum, and static from stray ground currents eliminated.

The correlation of the results of the tests outlined above, together with good coating practices and installation inspections, have indicated that thin-walled steel pipe can be satisfactorily used in the corrosive soils and stray current areas of urban centers.

Soluble Silicates for Corrosion Inhibition In the Oil Industry*

*By Wm. Stericker**

SOLUBLE SILICATES can be and, in some cases, are being used to inhibit corrosion, from the preliminaries of crude oil production to the delivery systems of the finished petroleum products. Sodium silicates are so inexpensive and yet so effective that the wonder is not that they are widely used, but why they are not used by many others in the oil industry. While soluble silicates is not the answer for all corrosion problems, it certainly is for a number of them. It sometimes seems that the low cost of the silicates is what prevents them from being more widely used. Certainly the silicate manufacturer is limited in his promotional activities by the small profits available. However, if the failure to use silicates is due to lack of knowledge, it is hoped this paper will offer evidence to enable others to use them.

The first plan for this paper was to start with drilling and follow through the steps of oil production to the finished products, showing how silicates had been or might be used to decrease corrosion. However, it soon became apparent that this method of treatment was too exhaustive and exhausting. Instead an attempt has been made to describe histories and to draw from them conclusions which will serve as guides in the use of silicates elsewhere.

Silicates and Silicas

Soluble Silicates

Before actually considering the first case, the materials which are to be used as inhibitors will be described briefly, because selection of the wrong silicate might result in the treatment being a failure. Soluble silicates which are in commercial use at present are mostly the sodium compounds, but potassium silicates are becoming important. So far as corrosion is concerned, only sodium compounds are considered at present.

The sodium silicates having the greatest inhibitory action are solu-

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Table I

Some Typical Sodium Silicates Used as Corrosion Inhibitors*

Manufac'urer's Designation	Na_2O Percent	SiO_2 Percent	Percentage Ratio	Molecular Ratio	Total Silicate Solids, Percent	Baume'
"N"	8.9	28.7	1:3.22	1:3.22	37.6	41.0°
"O"	9.2	29.8	1:3.22	1:3.22	39.0	42.2°
"D"	14.5	29.0	1:2.00	1:2.06	43.5	50.0°
"C"	18.0	36.0	1:2.00	1:2.06	54.0	59.1°
"Metso Granular	29.5	28.7	1:0.97	1:1.00	58.2	Granular Solid

* This list does not indicate the full range of sodium silicates available, only those which have been used to inhibit corrosion.

tions of glasses, which are made by fusing sodium carbonate with silica sand. These glasses are made to meet different standards in which the ratio of sodium oxide (Na_2O) to silica (SiO_2) varies from 1:1.60 to 1:3.75. Since the molecular weights of Na_2O and SiO_2 are very similar, the molecular ratios are approximately the same as the percentage ratios given. These sodium silicates are not definite compounds but glasses which dissolve to form colloidal solutions. A series of more alkaline, crystalloidal silicates are also known but generally they are less effective as corrosion inhibitors. The analyses and descriptions of some typical sodium silicates are given in Table I.

Forms of Silica

When sodium silicates are dissolved in water the silica may be present in at least four different distinguishable forms. These are:

1. Crystalloidal silica, which gives a yellow color with ammonium molybdate in acid solution. It is probable this class should be subdivided but there are no good methods for distinguishing subclasses.
2. Stable, hydrated colloidal silica, which does not give a yellow color with molybdate but which will not cause gelation to precipitate out of solution on long standing.
3. Unstable, hydrated colloidal silica, which is capable of causing gelation or precipitation in gelatinous form on standing without further treatment except aging and which is readily precipitated by slight changes in environment.
4. Unhydrated, or at most only slightly hydrated, silica which is not capable of causing gelation or forming gelatinous precipitates, but which settles out on standing. This form is readily visible in the ultra-microscope.

Form 2 is the most effective in the inhibition of corrosion, the form 1 is fairly good, the form 3 is poor, and the form 4 is without noticeable effect.

Salt Water

Brine Pipelines

In 1941, the author described[1] the savings which resulted when sodium silicate (N in Table I) was added to the brine in steel pipelines. This report can now be extended.

The first case was in Texas. Here,

in June 1938, the pipelines in a brine disposal system were found to be in very bad condition. Numerous sections of the pipe had failed and had been replaced. Test sections cut from the line at various points all showed bad corrosion; and it seemed that the entire system would have to be replaced within a year. The pipes had been installed in 1933 and the system started operating about the beginning of 1934. At the time the original installation was made, short sections of various kinds of metallic pipe were inserted for test, but all of them corroded badly. It was decided that the use of steel pipeline, with replacement when necessary, was as economical as any method.

Addition of Sodium Silicate

R. H. Fash, of the Fort Worth Laboratories, suggested that sodium silicate might provide a protective coating on the inside of the steel pipe used to carry the oil-well brine. We were asked to suggest the kind and amount of silicate to be used. Preliminary tests with some of the brine from the field indicated that under pipeline conditions, 40 ppm of soluble silica would give at least 80 percent protection and probably more. Therefore, the addition of 100 gallons of silicate of soda containing 8.9 percent Na_2O and 28.7 percent SiO_2 to each million gallons of salt water was suggested. When this silicate was added to the brine without dilution, a precipitate formed. If the silicate were diluted to 10 times its volume with fresh water before it was added to the brine, precipitation was avoided. There was no evidence of later precipitation at the high dilutions which actually existed in the pipeline. The method of feeding was simplified with the more dilute solution. The actual addition was made by means of needle valves on the suction side of the centrifugal pumps used to pump the brine.

Results Apparent After Two Hours

A test on one line was started June 4, 1938. Normally visible results are not expected in less than 30 days, but in this case improvement was evidenced in about two hours after the treated brine had filled the system. The brine, which had been bluish black with suspended matter in it, became colorless and free from turbidity. After 30 hours, sections of pipe carrying treated and untreated brine were examined. The corrosion scale had turned from a dull reddish brown to a light buff yellow. When magnified, the scale in the untreated line was found to be spongy, while that from the treated line was rough but tight. A drop of normal hydrochloric acid placed on the former was soaked up by the scale, with which it immediately reacted. On the treated scale it spread slowly and there was a lag of five sections before there was any evidence of reaction. Although the time had been too short for any scale removal, the silicate clearly had had a marked effect on the rust layer.

Treatment of all the lines in this particular system was started June 17, 1938. Six days later, which really was too short a time to see the full effect of the treatment, samples of brine were secured and compared with samples which had been taken

before the silicate treatment was started. The results are shown in Table II. These samples indicate why the most satisfactory method of studying corrosion under field conditions is examination of the pipe itself. The determination of the iron in the water or brine may indicate more or less corrosion than is actually taking place. This is particularly true in old piping systems where there is a possibility of removing former products of corrosion which appear in the liquid, thereby indicating a much higher rate of corrosion than is actually occurring. Conversely, if the products of corrosion are held on the pipe they will not appear in the analysis, but corrosion may be extremely severe, particularly if there is heavy tuberculation and pitting. In this case another variable was the amount of iron in the brine being fed into the collecting pits. For example, on June 3, 1938 there were 2.85 ppm as iron oxide, while on June 23 a sample taken at the same point showed 8.80 ppm. Some of this iron was removed and settled out in the pit. It would have required a number of samples to determine just how great this action was, but normally it would not be expected that it would be as great as is indicated in the table.

Table II
Characteristics of Treated and Untreated Brine

	Inlet, Collecting Pit	Outlet, Collecting Pit	End of Pipeline
6/3/38	**Before Silicate was Used**		
Time	9:00 AM	.....	8:30 AM
pH	7.3	.....	7.9
CO_2	13.1 ppm	.....	4.4 ppm
Alkalinity as $CaCO_3$	200.0 ppm	.....	200.0 ppm
SiO_2	15.0 ppm	.....	10.0 ppm
Iron as Fe_2O_3	2.85 ppm	.....	1.14 ppm
6/23/38	**After Silicate Treatment Started**		
Time	2:00 PM	2:00 PM	2:00 PM
pH	7.6	7.7	7.7
CO_2	13.0	6.5	6.5
Alkalinity as $CaCO_3$	210.3	199.4	199.4
SiO_2	11.0	27.3	13.3
Fe_2O_3	8.80	1.18	2.40

Scale Reduced 25 Percent in Seven Months

Examination of the pipelines was continued from time to time. After seven months it was estimated there had been a reduction of 25 percent in the amount of scale on the pipe. This not only increased the carrying capacity of the lines but reduced the resistance to pumping. The loose black material originally present had been removed and remaining scale was harder and more impervious. This was all covered with a characteristic thin, buff film. Some of the material which had been removed was deposited in the reservoir at the end of the pipeline, but no loose scale was found in the pipe itself.

Example of Low and High Dosages

At this time it was discovered that, because of a mistake, the same amount of silicate had been fed to all six pumps although two of them were pumping over twice as much brine as the others. The lines fed by these two pumps with the small dosage of silicate were examined and compared with pipes which had been fed with the larger dosage. The low dosage had not given the same degree of protection observed in the balance of the lines. These poorly protected lines had received not over 16 ppm of silica at any time. It had been planned originally to feed 40

ppm SiO_2 to the salt water. Actually, because of the failure of one shift to follow instructions, the average feed had been less. However, it was felt that sufficient film had been built up on the other four lines to allow some reduction in the feed to them. The dosage was adjusted so all six lines were to receive 30 ppm of SiO_2.

Results After 30 Months

Thirty months after the treatment was started a careful inspection of the system was made. The brine remained clear and colorless even at the outlet of the line. The corrosion scale which had been in the pipe at the time the treatment was started has been reduced to about half its original thickness. It was much harder and more resistant to the action of twice normal hydrochloric acid. As it came from the line it was black but when washed and dried it was found to consist of layers of corrosion products over the top of which was a firm coherent buff coating, which was not thicker than it had been 23 months earlier. This apparently is the material which acted to check the corrosion. It had considerable strength and in one place had formed a layer which prevented leakage through a hole the size of a lead pencil.

Almost as soon as the silicate feed was started, it was noticed that there were less leaks which had to be repaired. In the 29 months immediately preceding the use of silicate there were 218 leaks and in the first 30 months after the treatment was started there were 111. Included in the latter were 28 which were brought about by building up the pressure on the line deliberately so the weak spots could be located and repaired. There also were two which were known definitely to have been caused by external corrosion. As time went on, the number of repairs decreased in spite of the lines getting older and therefore being expected to give more rather than less trouble. In 1944, it was reported that there never was more than one break a month and that these were all due to external corrosion.

Economics of Successful Treament

This system of pipelines continued in active use until November, 1944. At that time disposal wells were put in a somewhat different location. Metal pipe was not available, so cement-asbestos pipe was used in the new system. The old system was used for the excess brine, which was about 3000 barrels a day in June, 1945. Eventually it is planned to use the old system as a standby when sufficient disposal wells are available to take all the brine from the field. Thus the pipelines which were to be discarded after four years of service without silicate treatment had lasted an additional six and a half years with much lower maintenance costs and were still in better condition than when the treatment was started. A major headache had been replaced by an operation which ran smoothly with the minimum of attention. Calculations show this result has been achieved at a cost for silicate of about forty cents per 1000 barrels of salt water[1].

Experience in other pipelines has been similar. The silicate has been added to the mixtures of crude oil and brine so as to secure the protec-

tive effect all the way through the system. There was some question whether this might result in emulsification but none was found.

Disposal Wells

One reason silicates have not been used more widely is that there has been a fear that calcium and magnesium silicates would be precipitated and plug disposal wells. Actually one such system has been operating with silicate treatment for between seven and eight years with no difficulty. It must be remembered that the concentrations of silicate used in this work are very low, so low they do not cause precipitation if added in the form of a dilute solution. (See Table I—1 volume of N to 9 volumes of fresh water). Actually the chance of clogging the wells with the products of corrosion is greater than with any silicate precipitate. Filters have been installed to prevent the iron oxide getting into the wells in some cases, but corrosion beyond this point may cause trouble if no treatment is used.

Costs will vary with the quantity of silicate purchased at one time and the distance from the nearest producing point. For example, this cost could have been reduced approximately one-third by purchasing in carloads.

If treatment is desirable after oil and brine reach the surface of the ground, it should have a protective effect "down hole." Actually this has been found to be the case in various fields. The silicate as delivered is diluted with at least nine volumes of fresh water and introduced into the well by means of a bleeder tube, or through the annular space between the tubing and the casing. An attempt is made to base the dosage on the amount of brine pumped. Again, it is recommended that about 40 ppm of SiO_2 or 100 gallons of silicate per million gallons of brine be used. (4 gals./1000 bbls.). In one case having particularly severe corrosion only one-tenth as many sucker rods had to be replaced after treatment as before. The tubing replacements were cut nearly in half.

Conclusions

From the foregoing it is evident that the addition of sodium silicate to oil brines, either before or after separation from the oil, protects the equipment used for handling and carrying these brines. The next thing to consider is what results have been obtained with waters containing little or no salt.

Fresh Water

Refinery Conditions

In 1940, experiments were launched in an effort to overcome general corrosion conditions throughout a large refinery. The water used for cooling was all handled in one large system. Forty-five thousand gallons per minute were sprayed in cooler towers with an average loss of about 6 percent, which included 2 percent blow-down to the sewer. The make-up water was about 2500 gallons per minute or 3.5 million gallons per day. Analysis of the water is given in Table III. Previous experience had shown that if the water were used without treatment, it formed scale. If three ppm of metaphosphate were used, the scale was

Table III

Analysis of Untreated Water Used in Refinery Cooling System

	Ppm
Calcium	14
Magnesium	4
Sodium	257
Silicon dioxide	26
Iron and aluminum oxides	1
Carbonates	20
Bicarbonates	414
Sulfates	29
Chlorides	147
Total Solids	912
Total hardness (Calculated as $CaCO_3$ equivalent)	48

This was a fairly soft water in which the principal dissolved solids were sodium bicarbonate and sodium chloride. The pH of the water was 8.5.

prevented but the system showed severe corrosion. In this system the water was piped in steel and the exchangers were steel with either steel or admiralty metal tubes. The phosphate solution was added to the flume leading to the circulating pump suctions. It was proposed to add diluted silicate at the same point. At the time the test was started the water temperature at the inlet was 87° F., and at the outlet 120° F. The maximum temperature reached anywhere in the system was 180° F., with the most severe corrosion at points where the temperature was between 110° and 140° F.

Silicate and Dosage

The minimum amount of silica naturally present in the well water used was 12 ppm. This concentrated in the system to about 26 ppm. It was pointed out that some of this might aid in protecting the system even though experience had shown that it was not sufficient in itself. Accordingly, it was recommended that nine ppm of SiO_2 in the form of "D" silicate (See Table I) be added on the basis of one-half the make-up water. The reason for this recommendation was that one-half the loss in the system was due to evaporation and therefore the silica from that portion should be retained in the system. A trial of only 10 days indicated that sufficient silica was not being added. It was recommended the dosage be increased from 400 pounds to at least 600 pounds and preferably to 800 pounds per day. The latter figure would add nine to ten ppm of SiO_2 to all the make-up water. "D" brand was selected for this treatment, first, because it is less likely to cause precipitation with calcium and magnesium on heating and concentrating, and, second, because it was felt that the additional alkalinity might help to convert the silica naturally present in the water to a form which would be effective in inhibiting corrosion.

After the dosage had been increased to 800 pounds per day, the silica content of the water in the system built up to about 47 ppm in about 20 days. During this period considerable silica was dispersed in the system, indicating that a protective film was being formed. An attempt was made to maintain 45 ppm of SiO_2 in the water by adding 600 pounds of "D" silicate. However, oil and gas leaks into the water continued. Large amounts of make-up water were added, apparently without changing the amount of silicate as the total SiO_2 in the system dropped to 27 ppm. Therefore, the dosage was again increased to 800 pounds per day, so the silicate content increased.

The results during this period were not very good. Both old and new tubes showed considerable cor-

rosion, as did the heads of the exchangers. It was suggested that a switch be made to "N" silicate (Table I) to see whether it would not form a protective film more quickly. It was also pointed out that the very frequent examinations, with scraping every time an examination was made, were disturbing any protective film which had been formed. This, of course, meant that each time a new protective coating had to be built up.

After using "D" silicate for four months, "N" silicate (Table I) was substituted. After a month and a half the SiO_2 in the system was 40 to 42 ppm. The results were still somewhat erratic but there was some evidence of improvement. However, as time went on the results became better and better, and this type of silicate has been used ever since.

Oxygen Content

At the time these experiments were started, it was pointed out that the only satisfactory method of judging results was to use portions of the system itself which could be examined at regular intervals. However, the refinery was equipped to determine oxygen losses and it was decided that these figures should be obtained for what they were worth. At the time there was a reduction in oxygen content from 4.8 ppm to 3.4 ppm on passing through the exchanger system. What happened in attempting to use this test is a good illustration not only of the danger of depending upon indirect figures, but of the type of thing which might occur to nullify results. There was a gas leak which resulted in large losses in oxygen. In the condenser in which the leak occurred, all the oxygen disappeared. The exact nature of the gasses was not known, but it seemed likely that they also increased the tendency to corrode. At any rate, at this time the oxygen determinations gave no indication of the actual amount of corrosion. Later when the leaks were eliminated there was no loss of oxygen in the system, the water in the outlet line being slightly supersaturated with oxygen. For example, approximately one year after treatment was started the return line showed 4.4 and 4.6 ml. of oxygen per liter of water at 112° F. and 108° F., respectively, on successive days. Saturation values are 4.1 ml. at 109.4° F. and 4.2 ml. at 107.6° F.

Test Condensers

At the time the test was started, four experimental condensers were installed at critical points in the system and the flow of water through them was regulated to be as nearly possible the same as through the regular condensers. Each of these had four tubes, one of each to be removed and replaced every two weeks, thus giving two- four- six- and eight-week trials. Experience showed that the shorter periods were too short. It was noticed that tubes which were exposed for two weeks showed more evidence of corrosion than those which had been exposed for longer periods. At first the headers on these experimental condensers were scraped every two weeks. This destroyed any film which had been formed; and gave only repeated tests of two weeks' duration. These tests confirmed previous conclusions that from 30 to 90 days' treatment

was necessary to give maximum protection. Later the tubes were exposed for longer periods and the headers were not scraped. One thing was clearly demonstrated by the experimental tubes; the tubes were much less corroded when they were exposed initially to water which was treated with sufficient silicate.

Results in the System

The best evidence of the effect of the silicate treatment was found in the actual operating units. Two months after the silicate treatment was started, a unit which had been in service for four months was torn down. Only 10 percent of the tubes were plugged with corrosion products. Previous to treatment, this unit had shown about 40 percent of tubes plugged in the same period of time. Condensers which were exposed continuously to silicate treated water had practically no plugged tubes so the periods between inspection were increased without trouble or danger.

After an eight-months treatment, the pipes to and from one plant condenser were inspected. The inlet line contained about one-eighth inch of corrosion scale with a number of small tubercles. This was covered with a buff film over a hard shell on the corrosion scale. The similarity to the condition observed in the brine line described earlier was marked. Exposure to the atmosphere for about a week did not affect the buff film or the hard shell but oxidized the ferrous compounds below, which had been exposed by cutting the pipe. The outlet line had evidently been installed nearer to the time when silicate treatment was started because it contained no corrosion scale, only the thin buff film. Before treatment, lines in these positions had both developed soft corrosion scale and tubercles.

In any plant test there is always the question whether the corrosive condition of the water has changed. Fortunately in this case we have the answer. Some new units were started in which raw well water was used. In a month corrosion was evident in one such unit. Silicate treated well water was then substituted for the raw water and apparently prevented all corrosion for the next two months. At the end of five months another inspection showed that, while a slight coating of rust had formed on the steel lines and steel condenser tubes, there was no pronounced corrosion and no pitting. This was also true of a toluene unit. The dosages used in these cases were 25 ppm of SiO_2 added as "N" silicate.

After 14 months one of the largest units was taken down for cleaning. On previous occasions this unit had been severely corroded and scaled. However, at this time the steel heads and water lines showed no evidence of active corrosion. The admiralty metal tubes and tube sheets looked very good with very little evidence of scale.

Savings in Replacement

The experiment was officially declared a success after 30 months. In 1940 when the silicate treatment was started a crew of three men were used at all times to keep the leaks repaired in this refinery. By 1943 corrosion had decreased to such an

extent that there were practically no replacements and this condition has continued since that time. When the silicate was first added the improvement in the water and in the condition of the pipes was gradual, but there has been a steady improvement through the years.

At the end of five years, the amount of make-up water added had increased to five million gallons per day, to which 2850 pounds of silicate were added. This was calculated to give about 20 ppm in the make-up water. The total silica content of the water including that originally present after circulation in the system averaged about 50 ppm. One hundred pounds of metaphosphate were used per day to maintain a concentration of two-thirds parts per million. The results seemed to be entirely satisfactory and the treatment has been continued.

Fresh Water

While the water used in this refinery was considered fresh, the chloride content at times when chlorine was fed to control algae rose to about 170 ppm. Even this much salt would increase corrosivity. On the other hand, it is probable that many refineries, because of tide-water locations, have similar concentrations of salt in their cooling water systems. While the results in this case were not as spectacular as in the case of the brine pipelines, it is believed the silicate treatment has proved its value in cooling water systems. This belief is supported by widespread use elsewhere in fresh water systems.

Acknowledgment

The writer is indebted to many people for the collection of many of the facts which have been presented here. Restricted approval of publication by the two companies involved in the cases discussed most fully prevents mentioning the names of the persons involved. This does not mean that we are any less appreciative of the help they have given us.

Reference

1. A.P.I., Div. of Production, Spring Meeting, Southwestern District, Feb. 1941.

A Message from Your Officers

This Month's Contributor
O. C. MUDD, Treasurer

THE word "Treasurer" brings to mind "money" or "dollars." That is most natural, and it is also natural that a treasurer be interested in money.

What is money? Basically, it is defined as a medium of exchange. Exchange of what? The exchange of something you have that others want or vice versa. The value of any effort or product offered for exchange depends upon the demand, and the demand is established by the benefits realized by those utilizing these offered services or products.

Creation of a demand for any service or product is most easily established by telling potential prospects about that which is available and benefits to be gained. Such demands are most often created by advertising presented as statements of facts, or by methods of direct or indirect appeal. Advertising is a means to an end only when something of value is offered. A sustained demand is established only after services or products have continued as a benefit to the user.

Corrosion prevention requires engineering services and products. The value of either or both are determined by comparison of results before and after applied mitigation measures where the corrosion cause remains unaltered, or by comparing simultaneous results under equivalent conditions with and without mitigation measures.

Mitigation measures, properly applied, have benefited many to date, and thus established a value. Competent corrosion engineers and conscientious manufacturers of equipment or products used in combating corrosion have something of value to offer those plagued with the ravages of corrosion.

Individuals may succeed in creating a demand for what they have to offer but greater advantages are gained through organized effort.

(Continued on next page)

The National Association of Corrosion Engineers, with its publication CORROSION, represents organized effort in the advancement of corrosion control and the creation of a demand for more extensive use of corrosion mitigation measures by presentation of dependable information to show the value of corrosion-control measures, and provides a direct means of advertising corrosion mitigation products or equipment to those most interested. This organized effort promotes sharing of experience and knowledge among those in this field of endeavor, thus increasing individual competence.

The true value of our Association is reckoned in a value of exchange and this value is created by effort—in plain language, it depends on work. The efforts of a few establish one level of value, the efforts of a greater number give an increase but the greatest comes only when all participate—when we have team work. Better team work is realized when individuals are personally acquainted. Personal acquaintance of all members in this Association is not possible, but an approach can be made through active functioning of Regional Divisions and Local Sections. Local Sections, particularly, promote personal acquaintance between members and discovery of where their efforts are most useful.

Thus the capabilities of individuals become known, and those with leadership qualities will advance to more responsible positions of organization work, to become acquainted with those from more remote localities. This, then, results in a relative acquaintance through the entire organization. The true value of our organization will be realized when individual capabilities are known and directed to obtain more rapid advancement.

Let us build a practical working organization, one that has something to offer as a benefit to others and the treasury will be assured of sufficient operating capital.

NACE News

TENTATIVE TECHNICAL PROGRAM FOR 1948 NACE CONFERENCE

Mars G. Fontana, Professor of Metallurgical Research, The Ohio State University, Columbus, and chairman of the Technical Program Committee for the 1948 Conference and Exhibition sponsored by the National Association of Corrosion Engineers, announced that, as of January 6, 34 of the 40 technical papers to be presented during the ten scheduled symposia on the program had been accepted, with acceptance of the six others expected momentarily. Four papers will be presented during each symposium, all of which will be held in Hotel Jefferson, St. Louis, Mo., concurrently with an All-Corrosion Show featuring the latest products, services, devices, and equipments in use today to mitigate and control corrosion. The meeting opens April 5 and extends through April 8.

The tentative technical program follows:

CATHODIC PROTECTION SYMPOSIUM

1. Twenty Years of Cathodic Protection in New Orleans, by R. J. Kuhn.
2. Cathodic Protection of Cross Country and City Gas Lines and also for City Underground Cables, by William J. Schreiner, The Cincinnati Gas and Electric Company.

3 and 4—Tentative.

CHEMICAL INDUSTRY SYMPOSIUM

1. Corrosion Problems in the Manufacture of Soda Ash by the Ammonia Soda Process, by Gustave Heinemann, Southern Alkali Corporation.
2. The Application of Electron Diffraction Techniques to the Study of Corrosion Processes, by Earl A. Gulbransen, Westinghouse Research Laboratories.
3. The Resistance of Alloys to Corrosion During the Processing of Some Foods, by J. F. Mason, Jr., The International Nickel Co., Inc.
4. The Corrosion of Aluminum in Dilute Aqueous Solutions, by John P. Howe, General Electric Company.

COMMUNICATIONS SYMPOSIUM

1. Current Intensities of Soil Corrosion Cells, by E. D. Sunde, Bell Telephone Laboratories.
2. Benefits to be Derived from Local Electrolysis or Corrosion Committees, by R. L. Lawall, American Telephone and Telegraph Co.

3 and 4. Tentative.

ELECTRICAL INDUSTRY SYMPOSIUM

1. Corrosion of Underground Power Cable Sheaths, by L. G. Greve, Commonwealth Edison Company.
2. Experience at Bagnell Dam to Prevent Corrosion of Underwater Steel and Iron, by Turner White, Jr., Union Electric Company of Missouri.
3. Corrosion from Flue Gases, by E. A. Rudulph, Steam Engineering Division Union Electric Company.
4. Paper on Corrosion and Combating Corrosion in Railroad Operations, by A. H. Archambault, Association of American Railroads.

GAS INDUSTRY SYMPOSIUM

1. External and Internal Corrosion Experiences of a Natural Gas Transmission Line, by N. K. Senatoroff, Southern Counties Gas Company of California.
2. Reference Electrodes, Design and Polarization Characteristics, by Raymond H. Hadley, Susquehanna Pipe Line Company.
3. Present Day Aspects of Condensate Well Corrosion, by Harry E. Waldrip, Gulf Production Division, Gulf Oil Corporation.
4. Tentative.

GENERAL INDUSTRY SYMPOSIUM

1. Corrosive Action of Natural Waters Throughout the Country, by F. N. Alquist, The Dow Chemical Company.
2. Cataloging of Corrosion Data, by Lorraine Voigt, The International Nickel Company.
3. The Behavior of Hydrogen in Steel During and After Immersion in Acid, by Lawrence S. Darken and Rodney P. Smith, Research Lab., U. S. Steel Corporation.
4. Corrosion Problems in Boiler Feed Waters and Waters Used in Plant Cooling Systems, by Sheppard T. Powell, Chemical Engineer.

OIL INDUSTRY SYMPOSIUM

1. Effects of Hydrogen Generated by Corrosion of Steel, by M. H. Bartz and C. E. Rawlins, Phillips Petroleum Co.
2. Action of Rust Preventitive Oils, by E. R. Barnum, R. G. Larsen, and A. Wachter, Shell Development Co.
3. Sour Crudes — Equipment Protection, by E. R. Camp, Humble Oil and Refining Co.
4. Tentative.

New Local Section

• ***Their petition for recognition as a Local Section of the Western Region of NACE granted, members of the Association who reside in the San Francisco, Calif., area, held a meeting and elected officers for 1948 as follows:***

Chairman: A. Wachter, Shell Development Co., Emeryville.

Co-Chairman: Peter C. Jurs, Shand & Jurs Co., Berkeley.

Secretary-Treasurer: W. R. Schneider, Pacific Gas & Electric Co., Emeryville.

PROTECTIVE COATINGS FOR METALS SYMPOSIUM

1. Principles of Protective Metals with Organic Coatings, by A. J. Eickhoff and William E. Shaw, National Lead Co., Research Laboratory.
2. Preparation of Metal Surfaces for Organic Finishes, by G. R. Hoover, American Rolling Mill Company.
3. Building Organic Protective Coatings to Special Requirements, by K. G. Compton, Bell Telephone Laboratories, Inc.
4. Organic Linings for Chemical Equipment, by Kenneth Tator, Industrial Lining Engineers, Inc.

SALT WATER CORROSION SYMPOSIUM

1. General Picture of Salt Water Corrosion Aboard Ship, by R. A. Pomfret and L. M. Mosher, Bethlehem Steel Company.
2. The Cathodic Protection of Steel in Sea Water with Magnesium Anodes, by H. A. Robinson, The Dow Chemical Company.
3. Performance of Steam Condensers Aboard U. S. Naval Vessels, by H. E. Bethon, U. S. Navy, Bureau of Ships, Navy Department.
4. Brine Corrosion in the Oil Industry, Gulf Research Development Co.

WATER INDUSTRY SYMPOSIUM

1. Corrosion Problems in Deep Wells, by T. E. Larsen, State Water Survey, Urbana, Ill. Discussion by representative of Electro Rust-Proofing Corporation.
2. A Survey of New Methods for Retarding Corrosion in Water Systems, by Linn H. Enslow, Editor, Water and Sewage Works, New York.
3. Economics Effected in Extending the Life of an Old 60 Inch Steel Pipe Line by Cementing in Place, by Centriline Corporation. Discussion by T. J. Skinker, Water Commissioner, St. Louis, Mo.
4. Retarding Corrosion in Water Systems by Proper Conditioning with Lime and Complex Phosphates, by John W. Ryznar, National Aluminate Corporation.

Though the Conference and Exhibition will officially get under way on Monday, April 5, the technical proceedings do not begin until the morning of Tuesday, April 6, when concurrent sessions will be held. No session is scheduled Tuesday afternoon, to permit more time for attendance at the Exhibition. Concurrent sessions will be held both in the morning and afternoon on Wednesday and Thursday.

As was the case last year, technical proceedings, exhibition and business meetings of the various committees of the Association will be held under one roof. Meeting rooms for technical sessions will be located on the Mezzanine Floor of Hotel Jefferson. The All-Corrosion Exhibition, which will be open daily from Monday through Thursday, will also be held on the Mezzanine floor of the hotel as will the Annual NACE Banquet, scheduled Wednesday evening, April 7, in the Gold Room.

The complete program will appear in the March edition of Corrosion.

GENERAL INTEREST

J. C. Stirling, Stanolind Pipe Line Co., Tulsa, Okla., has accepted an invitation to address the opening session of the 1948 NACE Annual Conference at Hotel Jefferson, St. Louis, Mo., on the afternoon of April 5. The Conference and Exhibition extends through April 8.

The Pittsburgh International Conference on Surface Reactions will be held at the Mellon Institute for Industrial Research in Pittsburgh, June 7-11, 1948. The conference Committee is made up of the following:

Earl Gulbransen, Westinghouse Research Laboratories, chairman representing The Electrochemical Society, Pittsburgh Section; D. S. McKinney, Carnegie Institute of Technology, representing the University Conference on Corrosion and Metal Protection; Mars G. Fontana, Ohio State University, representing the Electrochemical Society, Corrosion Division; J. M. Bialosky, Carnegie-Illinois Steel Co., representing the National Association of Corrosion Engineers; J. W. Hickman, Westinghouse Research Laboratories, representing the Pittsburgh Physical Society; C. Podocar, Mellon Institute, representing The American Society for Metals, Pittsburgh Chapter; George H. Young, Mellon Institute, representing The American Chemical Society, Pittsburgh Section; Richard Rimbach, Corrosion Publishing Co., representing The Corrosion Forum.

Preliminary plans call for technical sessions mornings and evenings, and visits to Pittsburgh research laboratories which are working on surface reactions, in the afternoons. Scientists, engineers and educators from many parts of the world have been invited to participate in the conference, and several will present papers.

Mars G. Fontana, professor of Metallurgical Research, Ohio State University, and member of the NACE Board of Directors, was the principle speaker at an executive committee meeting of the Carpenter Steel Company January 7, when that Reading, Pa., steel manufacturer announced a new "super corrosion-resistant" stainless steel. Mr. Fontana, who was immently associated with the development of the new alloy, which has been named "Carpenter Stainless 20," gave a constructive talk on the new alloy, describing the chemical composition, corrosion-resistant qualities, and mechanical specifications. He also outlined the various phases of its development. Other speakers on the program were J. H. Parker, president of the Carpenter Steel Company, and D. E. Jack, vice president of the Duriron Co.

PERSONALS

Ralph D. Parker and **J. Roy Gordon**, Copper Cliff, Ontario Canada, and **Herbert G. Fales**, New York, N. Y., have been elected assistant vice presidents of The International Nickel Company of Canada, Limited, according to Robert C. Stanley, chairman and president of the company. At the same time, Mr. Stanley announced the election of **Walter C. Kerrigan, James F. McNamara** and **W. T. Wickenden** as vice presidents of the company's United States subsidiary, The International Nickel Co., Inc.

Lachlan Mackenzie has been elected executive vice president of the Eastern Stainless Steel Corp., Baltimore, Md. He formerly served as assistant to the president and vice president.

Arthur G. Lambert is now vice president and manager of the Export Division, Atlas Steels, Ltd., Welland, Canada. Associated with the steel business in various capacities since 1919, he joined Atlas in 1940 as export manager. Previously he was with the Canadian Division of Jessop Steel Co., Washington, Pa.

Edward K. Davis resigned as director and president of New Aluminum Ltd., Montreal, Canada, which position he held since 1928; and has been succeeded by **Nathaniel V. Davis.**

Andrew Van Echo has joined the Wm. E. Pratt Manufacturing Co., Joliet, Ill., as metallurgical engineer. He formerly was technical service representative and chief inspector for Josyln Stainless Steel Co., Ft. Wayne, Ind.

Johan Bjorksten, president of the Bjorksten Research Laboratories, Chicago, Ill., has been elected to serve a two-year term as a director of the Association of Consulting Chemists and Chemical Engineers, Inc.

Robert G. Seyl, Chicago, Ill., has established the Seyl Laboratories in Chicago, specializing in the determination of corrosion factors of metals and solutions. Offices are located 221 N. La Salle St.

CORRECTIONS

Maurice W. Belson's name was inadvertently omitted from the NACE Membership Roster which appeared in the January edition of Corrosion, Vol. 4, No. 1, 1948. Mr. Belson's name should have appeared in the section covering Shreveport, Louisiana, and as associated with D. E. Stearns, with the address of Post Office Box 1234.

The company affiliation of T. M. Riseling, listed under Oklahoma City, Okla., should read Cathodic Servicing Company, Box 3737, and not as printed.

The company affiliation of Messrs. H. W. Foelsch and C. L. Ziemann, listed under Chicago, Ill., should read Stalpic Coating Corporation, 1128 W. Armitage Avenue.

NEW PRODUCTS, MATERIALS AND SERVICES

A gage which quickly reads thickness of wet films has been developed by the Interchemical Corp., Finishes Division, and is being distributed by Henry A. Gardner Laboratory, Apparatus Division, Bethesda, Md. The gage is operated simply by rolling it over the wet film, and thickness is read directly on a 0 to 4 mils calibrated scale engraved on the outer wheel of the instrument. An accuracy of 0.0001 inch is claimed. No larger than a man's pocket watch, the instrument is constructed of stainless steel. Measurements can be made on simple concave and convex surfaces. A 0 to 2 mil gage is being developed to facilitate measurement of thin films.

Field and laboratory tests conducted since late 1943, indicate that Coro-Gard, a newly-available coating developed by the Minnesota Mining and Manufacturing Company, will prevent corrosion of steel tanks in sour crude service for at least two years, probably longer, the producers announced. During service life, the coating in some instances would require retouching at about two-year intervals. Application requires 48 to 96 hours for average tank, including cleaning, spraying on of three coats and curing. First used as a sealant for aircraft jettison tanks, the coating was later shown to be effective in protecting steel against corroding action of sour crude, salt water, acidic salt solutions, and the Butterworth cleaning system. Tests were carried on over a four-year period in sour crude fields, including the Midland-Odessa, Texas, Field. Coro-Gard has a synthetic resin base, a powdered gray pigmentation, and a solvent consisting of methyl-isobutyl-ketone and butyl acetate, 1:1 by volume. A black variation is achieved by added two percent carbon black. Solids content is approximately 26 percent. Viscosity corresponds to a thin syrup—3-5 at 80° F., on a No. 26 wire of MacMichael viscosimeter. Application is by conventional spray, brush or slosh, and involves no activators, heat cures or primers. Complete information on the new coating can be secured by writing the manufacturer at 900 Faquier Ave., St. Paul 6, Minn.

A "palm-size" hose valve has been developed for use in a variety of industries, from chemical plants to breweries and food and drug product manufacturer. Designed and produced by the Paul Valve Corporation, 683 Third Avenue, New York, N. Y., the valve features rust-proof construction, and ease of operation. At 50 psi hose pressure, less than 10-pounds finger pressure on the release button is required to open the

valve. Only four pounds pressure are required to hold it open, to maintain a flow of approximately 13 gallons per minute through the nozzle. The valve is available for standard hose size from one-quarter inch to one inch, delivering 13 gallons per minute at 75 pounds per square inch pressure. It is made entirely of Monel for maximum resistance to corrosion and wear.

Flagg-Flow malleable pipe fittings, said to be the first threadless malleable fittings made for brazed pipe joints, have been introduced by Stanley G. Flagg & Co., Inc., Philadelphia, Pa. Elimination of thread cutting is said to open the way for the reduction of pipe wall thickness, and weight of pipe. Designed for brazing to standard black steel and wrought iron pipe, the new fittings are currently made in sizes up to and including two inches. These threadless malleable fittings are applicable wherever 150-pound standard weight black, malleable, screwed fittings are now used; that is, for 150-pound working steam pressure at 450° F., or 300 pounds, non-shock, oil water or gas lines at 150° F.

Micro Metallic Corporation of 193 Bradford Street, Brooklyn 7, New York, announces production of "in-line" filters fitted with porous stainless steel filter elements. Filters are provided with interchangeable porous stainless steel elements of various types. Removal of a filter element and replacement with another of different porosity or type can be accomplished within a matter of seconds. Fluid passageways are all readily accessible for cleaning. All connections are standard pipe threads. Quick disassembly and assembly is accomplished by use of rapid acting forged steel swing clamps for closure. All working parts are forged or rolled stainless steel. The filter bodies are normally supplied for 200 pound service, but units rated for higher pressure are available. Porous stainless steel filter elements are provided in a variety of of shapes and sizes. Three principal types are provided; cylindrical, bayonet, and star type. Cylindrical elements are not generally recommended where large pressure differentials are encountered, although these can be reinforced to withstand up to 1000 pounds or more differential pressure. "Bayonet" shaped elements can be more inexpensively reinforced for any high pressure work, and are regularly supplied with a 100-pound differential rating; these bayonet type elements also have less hold-up and provide more space for solids collection than the cylindrical type. Star-type filters are provided for the two larger sizes and their corrugated surface provides a maximum of filter area, and these units are therefore ideal for large "clarification" or "polishing" installations. Where a large volume of solids is to be collected, modified "star-type" elements are provided. Due to workable self-supporting nature of the stainless steel porous elements, extraneous supports are eliminated, and the resulting filter is comparatively more compact, more convenient in use, and more economical. Units are available with filter areas ranging from 18 square inches to 24 square feet in pipe sizes from ¼" to 1½". Pore openings of the porous stainless filter elements range from 20 to 65 microns.

USEFUL BOOKS LITERATURE AND PAMPHLETS

Spang-Chalfant Division, The National Supply Co., Toledo, Ohio, have published a 22-page booklet describing the problem of corrosion fatigue, its economic considerations, and of development of plastic-coated drill pipe for drilling oil wells in highly corrosive fields. The descriptive material, illustrated by 12 photographs, explains the development of the new pipe, reason for selection of thermosetting plastic, results of field and laboratory test program, and the story of its manufacture.

A compressed handbook and guide, "Nickel and High Nickel Alloys," is being distributed by The International Nickel Company. Written by Dr. Norman E. Woldman, consulting metallurgical engineer and former Chief Metallurgist for Bendix Aviation Corporation, it originally appeared in the technical press and has been made available in convenient reprint form. In addition to information on nickel, Monel, Inconel, and associated alloys it also includes material on such other alloys as the Hastelloys and Illium. Dr. Woldman reports on properties, heat and corrosion resistance, as well as on modern fabrication and finishing practices. It will be sent on request to The International Nickel Company, Inc., 67 Wall Street, New York 5, N. Y.

Colville, Ltd., 1945 West George Street, Glasgow, C.2, Scotland, have available a 24-page booklet describing creep resisting qualities of Colmo steels for high temperature service. Graphs, tables and specifications on various types of steels produced by the company list characteristics.

A. M. Byers Co., Pittsburgh, Pa., have prepared a 20-page illustrated booklet describing the "ABC's of Wrought Iron." The booklet tells in non-technical terms what wrought iron is, why it resists corrosion and withstands shocks and vibration, how it is made, bent, welded and treated.

A complete listing of commercial and university testing and research laboratories throughout the country, together with indications of the type of commodities tested, has been compiled by the National Bureau of Standards. The pamphlet is available from the Government Printing Office as NBS Miscellaneous Publication M187, entitled Directory of Commercial and College Laboratories. Information is given concerning 220 commercial laboratories, with 80 branches or offices, and 189 colleges laboratories used for research and testing as well as instruction. Listings are both geographically and alphabetically arranged. Obtainable at 30 cents per copy from the Superintendent of Documents, Washington, D. C.

Corrosion Abstracts

ATMOSPHERIC CORROSION

Atmospheric Corrosion in Seaports. R. SCHAUDER, S. African Mining Eng. J. **57,** 541 (1947); Chem. Abs. **41,** No. 8, 2379 (1947) April 20.

Under the very bad conditions prevailing at Port Elizabeth and the South African East Coast, iron roofing material and the chrome-plated fittings of motor cars, fence posts, and fencing wires are soon destroyed. As a remedy, asbestos, lead, and copper are recommended to replace iron, and also aluminum in place of chromium-plated fixtures and for roofing.—INCO.

Atmospheric Corrosion of Iron and Steel. F. C. STRONG, Cedar Crest College, Monthly Rev., **34,** No. 5, 551-556 (1947) May.

Summary of present-day knowledge of atmospheric corrosion of iron and steel for the worker in metal finishing. Author gives some definitions and discusses corrosion by moist air and atmospheric impurities, and protection of iron and steel by composition change (addition of nickel or chromium and nickel making it stainless steel), and natural and artificial protective coatings. 12 references.—INCO.

BOILER CORROSION

Facts and Factors of Boiler Corrosion. K. R. HODGES, Ind. Power, **52,** 88-89 (1947) May.

Effects of overheating as well as chemical, electrchemical, and galvanic action which cause common corrosion difficulties discussed. Includes table of minimum air-heater metal temperatures for stoker, pulverized-coal, and oil firing, and emphasizes necessity for avoiding dewpoints of flue gasses.—BLR.

Causes of Corrosion in High Pressure Boiler Tubes. PAUL M. BRISTER & J. B. ROMER, The Babcock and Wilcox Co., Petro. Engr., **18,** No. 8, 60 (1947) May.

For high temperature superheater tubes, the paper shows how temperature shock affects the rate of corrosion on the steam side and the gas side of the tube. With proper selection of ferritic type chromium-molybdenum steel alloys, steam and flue gas corrosion is not troublesome for metal temperatures up to about 1200° F. Stainless steels are satisfactory for structures somewhat above 1200° F. For structural members, such as hangers and supports, chromium-nickel steel alloys are pre-

ferred for elevated temperature service. A type of corrosion that has been quite serious, although not prevalent, in carbon steel tubes in high pressure boilers appears in the form of intergranular disintegration of the metal adjacent to a pit that is filled with iron oxide. Usually deposits of metallic copper, and oxides of copper are present in the zone affected by corrosion, but authors point out that metallic copper is often found in boilers not troubled by corrosion. Dissolved ammonia in boiler feedwater can bring copper into the boiler, from contacting materials containing copper. Hence, ammonia in feedwater should be reduced as much as possible; the boiler water should be maintained at a satisfactory pH; the dissolved oxygen should be reduced to as nearly zero as possible and an excess of sulphite maintained in the boiler water. Oxygen and copper are believed to be the causes of this trouble. Severe corrosion in superheaters appears to come about as follows: (1) A thin, tightly adherent, oxide deposit forms on both the steam side and the gas side of the tube wall; (2) Temperature shock of the relatively low temperature steam or steam and water from deslaggers causes cracking of oxide due to different thermal expansion characteristics of oxide and metal; (3) The surface exposed at the base of the cracks become oxidized; (4) This cycle is repeated many times; (5) The layer of oxide on the inside metal surface raises metal temperature in the tube, thus increasing oxidation rate; (6) Progressive oxidation from both the inside and outside of the tube wall reduces thickness of wall, and increases stress; (7) The increased temperature reduces the strength of the metal, which together with increased stress causes accelerated creep of the metal; (8) The accelerated creep continues until failure occurs. Authors concluded that chromium-molybdenum steel alloys contained from 2-9% chromium and 0.5 to 1.0% molybdenum when properly selected for the expected temperatures are very satisfactory for use with metal temperatures up to 1200° F. Above this temperature it appears that the stabilized 18-8 stainless alloy is satisfactory.—CEC.

External Deposits on Boiler Heating Surfaces. Combustion, **18,** 26-28 (1947) May.

A digest of a report issued by the British Boiler Availability Committee covering an investigation of the form and composition of deposits in a large number of boilers examined. The mechanism of deposit formation was investigated and is discussed; and the behavior of sulfates, bisulfates, phosphates, and chlorides was studied, particularly chemical changes taking place in the vapor phase.—BLR.

A Note on the Selective Corrosion of Phosphor Bronze in Hot Water Service—Paper 1048. W. D. CLARK. J. Inst. Metals, **73,** Part 5, 263-271 (1947) Jan.

Phosphorus bronze pump impellers handling hot feed water and condensate on a power station appeared to corrode similarly to dezincification. Microscopic, chemical and X-ray analysis showed the phenomenon to be due to penetration of zeolite-softened feed water into por-

cus sections of the casting and resultant formation of particles of copper and stannic oxide. The attack at machined surfaces was much greater than that at "as-cast" surfaces. On the "as-cast" surface, the attack had progressed in a complex manner, leaving a number of lamellar residues.

Internal Corrosion of Furnace Tubes of High Pressure Boilers. RICHARD C. COREY. Combustion, **18,** 39-42 (1947) Mar.

An extended discussion of experiences with internal tube-corrosion at Springdale and Firestone, which were reviewed in the December, 1946, issue. Additional data are tabulated and charted.—BLR.

Some Experiments on Corrosion of Steel by Boiling Water. A. J. GOULD AND U. R. EVANS. J. Iron & Steel inst., **155,** 195-200 (1947) Feb.

Behavior of steel in boiling water is shown to be determined largely by the position of the solid corrosion products formed. Under anaerobic conditions steel reacts at first with water, eliminating hydrogen, but a film is formed over the surface, so that the attack over long periods is very slight. In presence of oxygen the conversion of ferrous hydroxide to magnetite, or rust, appears to take place to some extent at a distance from the metal, so that the film is discontinuous, and serious corrosion occurs. Salts tend to increase, and sodium hydroxide to diminish, the attack under aerobic conditions. Copper deposited on part of the steel increases the intensity of attack in short experiments but not in long ones.—BLR.

Corrosion of Iron in Neutral Solutions. A. I. KRASILSHCHIKOV. J. Gen. Chem. (USSR) 543-50 (1946); Chem. Abs. **41,** 4, 941 (1947) Feb. 20.

It was shown that iron dissolves to a measureable degree in water and in neutral solution even in the absence of oxygen. The reduction of oxygen and separation of hydrogen occur on different sections of the iron surface. The concept of very high local potentials is used to discuss the phenomenon of pitting corrosion.—INCO.

Starch Prevents Scaling in Navy's Evaporators. CARL J. LAMB. Chem. Ind., **60,** 411 (1947) Mar.

Suggests that colloidal starch, which solved the Navy's evaporator-scale problem may be of benefit to chemical plant installations using sea water.—BLR.

Inhibition of Hard Scale in Boilers, and the Action of Static Charges Upon Colloids. E. J. B. WILLEY. J. Soc. Chem. Ind., **65,** 12, 433 (1946) Dec.

Two methods claiming to give remarkable results in the treatment of feedwater are: 1) an electrode system through which the water circulates under a field of a few millivolts, and 2) an assembly of glass bulbs containing mercury where static charges develop externally as the mercury is caused to move about by flow of water are described. The reaction seems to involve colloids present, these being enabled to undergo strong adsorption at the surface of nascent crystals and, although present in very small amounts, give rise to development of other crystalline forms that normally appear only when large

amounts of "boiler fluids" are used in absence of either of these devices. Static charges seem able to exert a profound influence upon the rate of reaction of one colloid with another, positive sols being made more reactive towards negative forms, and conversely.—INCO.

Steam Turbine Lubrication Problems and Their Solution. Part 3. ALAN WOLF. Petro., **10,** 30-31 (1947) Feb.

Discusses the cooling function of the oil, tube-corrosion problems, and use of rust inhibitors. (To be continued.)—BLR.

Corrosion-Erosion of Boiler Feed Pumps and Regulating Valves. H. A. WAGNER, J. M. DECKER, & J. C. NASH, Trans. ASME **69,** 389-403 (1947) May.

Seven 500-hour corrosion-erosion tests, involving 18 different materials, were conducted at the Marysville power plant of Detroit Edison Co. to determine resistance to corrosion-erosion attack. Results are given in detail.—BLR.

Investigation of Acid Attack on Boilers and the Effect of Repeated Acid Cleaning on the Metal. H. C. FARMER, Trans. ASME, **69,** 405-412 (1947) May.

Investigation shows that stressed metal is more readily attacked by inhibited acid than stress-relieved metal. With a knowledge of the controlling factors, such as temperature, acid strength, and contact time, the operator can acid-clean boilers with a reasonable assurance that corrosion or metal attack will be reduced to a minimum.—BLR.

CATHODIC PROTECTION

Natural Gas Stored in Buried Pipe at 2240 Pounds. C. R. CLAXTON, Stone & Webster Eng. Corp., and M. G. MARKLE and D. V. MEILLER, Pub. Serv. Co. of Northern Ill., Oil & Gas J. **45,** No. 43, 60+ (1947) Mar. 1.

Fifty lengths of 24-inch pipe, 40 feet long were made up with ends swaged down for 1—½ pipe connections. Four of these pipes were connected in series and to a common manifold. Although threaded joints were used, most of these were later welded. All of these pipes and connections were then coated and provided with cathodic protection. The ground cover was 3 feet 6 inches. The storage capacity of these pipes was found to be 40% in excess of that calculated by the simple gas laws, and very much in excess of the air capacity at the given pressure. A compressor was used with a capacity of 6000 cubic feet per hour. No after cooling was provided, but provision was made for heating the compressed gas prior to expansion. This installation was to supplement existing holder and water gas plant so as to give time for emergency repairs to the transmission main. Total storage capacity of this installation was 1,250,000 cu. ft. at ntp.—CFC.

Galvanic Aluminum Anodes for Cathodic Protection. R. B. HOXENG, E. D. VERINK, & R. H. BROWN, Corrosion **3,** No. 6, 263-274 (1947) June.

Laboratory and service data indicate that the technical development of galvanic aluminum anodes in wet and packaged backfills has been successfully directed towards (1) increasing anode-to-soil potential, (2)

decreasing anode-to-soil resistance, (3) increasing ampere hours per pound. At the present stage of development it is believed that aluminum anodes will give at least 675 ampere hours per pound in properly prepared packaged or wet backfills. At 675 ampere hours per pound, one pound of aluminum does the work of 1.12 pounds of magnesium or two pounds of zinc. The relative metal cost per ampere year for aluminum, magnesium, and zinc is as follows:

METAL	Ampere Hours per Pound Estimated	Pounds of Metal per Ampere Year	Price Factor
Aluminum	675	13.0	1.00
Magnesium	600	14.7	1.62
Zinc	335	26.2	1.81

(Based on currently quoted anode prices in carload lots.)

On this basis, it is apparent that light metals can supply current more economically than zinc. Obviously, in addition to metal cost, the installation costs must be included in determining the total cost per ampere year. By using packaged anodes, substantially reduced installation costs are anticipated. Development work now in hand gives promise of more ampere hours per pound and of improved packaging techniques, hence it is not unreasonable to expect further improvement in cathodic protection by using galvanic aluminum anodes.—ALL.

Relative Effectiveness of Cathodic Protection and Painting in Preventing the Corrosion of the Interior of Steel Tanks. T. W. HISLOP, JR., Am. Railway Eng. Assoc. Bull. 462, 196-201 (1946) Nov.

A progress report showing how cathodic protection may be applied to tanks. So far, it has proved more effective than paints.

CHEMICAL CORROSION

Investigation of Acid Attack on Boilers and the Effect of Repeated Acid Cleaning on the Metal. H. C. FARMER, Phila. Electric Co., Trans. ASME, **69,** 405-12 (1947) May.

To minimize corrosion in acid cleaning of boilers with hydrochloric acid inhibited with Dowell A-12, the following recommendations are made after extensive laboratory tests: (1) cleaning solution temperatures should not exceed 140° F.; (2) an acid concentration of 5% is desirable, using two stage operations, rather than stronger solutions if the deposit is heavy; and (3) the contact time should not exceed 6 hours. It was also found that unstressed or stress-relieved metal shows a lower metal loss than stressed metal. Observance of these precautions enables the operator to acid-clean boilers with the assurance of reduced corrosion or metal attack. Test procedures, chemical reactions involved and their results are discussed.

Chemical State of Surfaces and Passivation of Mild Steels of Low Alloy Content. E. HERZOG. Metaux Corrosion-Usure, **20,** 127-134 (1945) Oct. (In French.) Metals Rev. **20,** 1, 18 (1947) Jan.

A new method of surface treatment of mild steels and steels with low alloy content to induce passivity of such surfaces is proposed. The method consists of preliminary dipping in nitric acid followed by dichromate treatment for 10 to 15 min. at 100° C. Passivity disappears when the surface is heated above 60° C.

Corrosion of Metals—New Phosphating Methods of Protection. W. G. Cass. Cham. Age. **54,** No. 1397, 373-374 (1946); J. Inst. of Metals and Metall. Abs., **14,** 56 (1947) Feb.

A review of recent improvements in the phosphating of iron, steel, and other metals, particularly in America and Germany is given.—INCO.

A Surface Active Agent for the Cleaning of Metals. O. M. Morgan. The Monthly Rev. Am. Electroplaters' Soc. **34,** 4, 430-441 (1947) Apr.

A synthetic organic detergent of the alkyl aryl sodium sulphonate type, sold under the trade mark "Nacconol NR," is shown to cause a definite improvement in the metal cleaning efficacies of alkalis and acids. (See also U. S. Patent No. 2,314,285.) Through the use of this product, treatment time, operating temperatures and concentrations of chemicals can be reduced. Its cleaning ability is not affected by the hardness of the water. A new quantitative method has been developed for the evaluation of metal cleaning compounds. Since mineral oil fluoresces brightly under ultraviolet light and fluorescence is capable of being photographed, a convenient means is provided for the detection and recording of oil residues on metal surfaces both before and after cleaning.—ALL.

Reaction of Moist Hydrogen Halide Vapors on Metals. W. Feitknecht, Helv. Chim. Acta, **29,** 1801-15 (1946) (In German); Chem. Abs., **41,** No. 5, 1193-1194 (1947) March 10.

Visual examination and x-ray diffraction studies were used to follow the course of the reaction of air containing vapors of hydrogen-chlorine or hydrogen-bromine on zinc, cadmium, nickel, and iron, and to determine the rate of attack. For the initial stages of the attack, the reactivity of the surface oxide layer is the determining factor. Oxide films on nickel and iron react only slowly or not at all with dilute acid vapors with the formation of basic salts. Attack starts at weak points in the film and spreads. In later stages of corrosion, electrochemical processes become predominant. Solid reaction products may be hydroxides, basic salts or normal salt. Each is discussed. A very low effectiveness (defined as the ratio of the weight of corrosion product actually formed to the theoretical) is found when the oxide film is very resistant to attack, as with stainless steel.—INCO.

Graphite Heat Exchangers, Parts I and II. C. E. Ford, National Carbon Co., Chem. Eng., **54,** No. 1, 92-96 (1947) Jan.; No. 2, 132-135 (1947) Feb.

Physical, thermal and corrosion-resistant properties of impervious graphite reviewed, its reaction to specific chemical reagents tabulated, and design and operation of graphite heat exchangers discussed. Impervious graphite possesses the unusual combination of chemical inertness and high thermal conductivity. Mechanically, it may be compared with grey cast iron. Material is much stronger in compressive strength than in t.s. and there is practically no elongation under tension. Equipment must be lined up to fit without resorting

to bending or springing of the parts into place. Maximum pressures and temperatures are mentioned. Impervious graphite was used to replace Monel coils in heaters handling slurries of ammonium sulphate. The latter are attacked at the cold end by successive erosion by crystals on the protective film of the metal and then directly by solution. At the hot end, the breakdown is caused by straight corrusion due to high temperatures. Performance design and construction are briefly summarized for acetone condensers, HC_1 reboilers, HCl and $AlCl_3$ reboilers, H_2SO_4 dryer precoolers, alcohol and hydrogen-chlorine condensers, tetrachlorethane condensers, hydrogen-chlorine HCN SO_2 and H_2O condensers, electrolyte heaters and viscose spin bath evaporators.—INCO.

COATINGS

Bituminous Coatings for the Protection of Iron and Steel Against Corrosion. R. St. J. Preston, DSIR Chem. Research Special Report 5, 1946, 39 pp. BNF Serial 29,876.

A survey of information. Bituminous coatings are classified in respect of their media and pigments; their value for protection of iron and steel against corrosion, particularly under immersed conditions, is critically reviewed. A survey of compositions used for protection against fouling by marine organisms, an ancillary problem to that of corrosion prevention, is included. 256 references.—BNF.

Preparation of Metals for Painting—A Review. R. E. Gwyther. Corrosion **3**, 4, 201-207 (1947) Apr.

Discusses the effective use of paint as a means of protecting metals from atmospheric corrosion, and the required preparation of different metal surfaces prior to application of paint. With respect to aluminium, three types of simple chemical treatment are detailed. As to magnesium, normal atmospheres have little effect thereon other than discoloration. Most magnesium products are finished with a protective chemical coating, which is intended to protect the metal during storage, shipment and manufacture. The chrome pickle process, known as Dow No. 1 or AMC "A," is used for this purpose. The treatment comprises a short immersion in a solution of nitric acid and sodium dichromate. The coating is suitable as a paint base but cannot be used where close tolerances are required, due to etching of the metal. The dichromate process, known as Dow No. 7 or AMG "G," is the best one for corrosion resistance. The method is as follows: 1) solvent, vapour, or emulsion cleaning; 2) alkaline cleaning; 3) immerse in hydrogen-fluorine solution (10 to 25 percent); 4) cold water rinse; 5) immerse 45 minutes in dilute sodium dichromate; 6) rinse cold and hot. Magnesium can also be anodised, producing a coating which has excellent corrosion resistance. Probably the best known method is Navy PT-13d Process.—ALL.

An Accelerated Method of Electrolytic Polishing. L. Chamagne, H. Granjon and A. Leroy. Metaux & Corrosion, **21**, 250, 73-80 (1946) June.

Time required for electrolytic polishing is reduced by applying a high voltage to specimen at moment of immersion and then reducing this

voltage as the required potential difference builds up across cell; a simple apparatus is described. Polishing takes about 20 seconds, which is advantageous in examining non-uniform specimens, such as welds, which might otherwise corrode. Micrographs of aluminum-magnesium, aluminum-magnesium-silicon and steels are shown.—BNF.

Electrolytic Polishing — Parts I and II. P. A. JACQUET. Paper before Soc. Francaise de Metallurgia. Metal Ind., **69,** No. 13, 263 (1946) Sept. 27; Ibid. No. 14, 304 (1946) Oct. 11.

Electrolytic polishing as a technique for metallographic specimens is discussed in detail. Examples with copper specimens are cited. The basic method and modifications are reviewed with references. Among other claims, more reliable estimates are said to be made of the oxygen content of copper than by mechanical polishing. The presence of copper sulphide inclusions in OFHC copper was discovered the first time this way. Use of electrolytic polishing to reveal slip lines is discussed in the second installment.—INCO.

Protective Finishing of Electrical Equipment. F. WIDNALL & R. NEWBOUND, Inst. Elect. Eng. Preprint, for reading Feb., 1947, 11 pp. BNF Serial 29,910.

Review of current practice and methods. Conditions of service (outdoor, industrial, domestic, marine and others); methods (electrodeposited coatings, chemical finishes, paints, sprayed metals, vitreous enamels); applications of various methods under various conditions; testing and control of finishes.—BNF.

CONSTRUCTION MATERIAL

Wet and Dry Chlorine vs. Materials of Chemical Plant Construction, Parts I, II and III. Chem. Eng. 54, No. 1, 211-212, 214 (1947) Jan.; No. 2, 219-220, 222 (1947) Feb.; No. 3, 213-214, 216 (1947) Mar.

First installment of this summary by manufacturers includes lead, high-silicon irons, chemical porcelain; second covers vitreous silica, Worthite, tantalum, silicones, rubber lining, glass-lined steel, carbon and graphite, Hastelloy (by C. G. Chisholm, Haynes Stellite Co.) wood tanks; last installment includes Durimet, Chlorimet, nickel and nickel alloys (by W. Z. Friend, Inco), chemical stoneware. Corrosion data are tabulated for Monel, nickel, Inconel, various types of nickel-resist. —INCO.

Purchase and Maintenance of Deep-Well Pumps. L. J. ALEXANDER. J. AWWA, **38,** 1197-1207 (1946) Oct. Corr. & Mat. Prot., **4,** No. 2, 24 (1947) Mar.-Apr.

Includes discussion of corrosion of turbine pumps. Causes are chemically corrosive waters, entrained gases, bacteria; and difference in electric potential between parts of the unit. In extreme corrosion, the best preventive measures are to use a stainless-steel shaft, bronze bowls and impellers in the bowl assembly, a 5-ft. section of bronze oil tube, a stainless steel line shaft from bowls to static water level, and a coating of coal-tar enamel outside the oil tube and inside and outside the eduction pipe. Discussion is devoted entirely to experiences with corrosion of pumps in Illinois and methods of prevention. Types of attack which have been recognized are gal-

vanic action, waterline corrosion, carbon-dioxide corrosion, and stray currents.—INCO.

Equipment and design — Metal Filters. C. O. Brown, Ind. & Eng. Chem., **39,** No. 2, 71A (1947) Feb.

A new filter medium composed of various stainless steels is offered by The Micro Metallic Co. of Forest Hills, N. Y. Bars of 18-8 with and without molybdenum, 20-12 nickel, and molybdenum-nickel alloy are first heat-treated and then disintegrated to powders in which each grain has the true alloy composition. These powders are sized into several uniform grain sizes and molded into sheets or special shapes for direct mounting into the filter frame. It is easy to obtain a medium having mean pore openings from 4 to 165 microns. When such filters are subjected to a differential pressure of 10 pounds psi, one square foot will pass 2 to 750 gallons/mm., respectively. As the all-metal material is strong and rigid, the filter can be cleaned by a relatively fast, high pressure backwash. The pure alloy construction enables this filter to handle hot concentrated nitric and sulfuric acid and sodium hydroxide solutions. Filters are shown.—INCO.

New Strong, Non-Magnetic Spring Material Has High Corrosion Resistance. Materials & Methods, **25,** 94-95 (1947) Apr.

Elgin watchspring material is strong, relatively hard, nonmagnetic, highly resistant to corrosion, nonsetting, and otherwise superior to high quality carbon steel spring materials. Comparison of the properties of Elgiloy with those of the carbon steel spring material shown.—BLR.

FUNDAMENTALS

Electrochemistry of Protective Films on Metals. A Study of Films on Aluminum and Phosphated Iron. G. V. Akimov & E. N. Paleolog, Comptes rendus de l'academie des sciences (USSR), **51,** 295-298 (1946), Chem. Abs. (USA), **40,** 7011-7012, 551.1 (1946) Nov. 20.

The work was undertaken to develop a simple electrochemical method of establishing the film structure assumed. A nonconducting protective film on a metal surface may consist of (1) electrochemically inert areas with relatively thick spots; (2) cathode areas with spots of small thickness through which electrons may pass; and (3) anode areas with pores, cracks, and weak spots. A metal specimen covered with a film was placed in an electrolyte solution containing a cathode or anode indicator, where it was subjected to polarization. The film surface was constantly examined with a microscope of 50-150X. Phosphated iron was subjected to weak anodic polarization in a solution consisting of 20 cc of 1 per cent potassium ferricyanide, 172 cc of 1 normal sodium sulfate and 8 cc of 0.1 normal sodium chloride. The anodic areas were detected in the form of dark blue elevations. The electrolyte was then replaced with a solution of normal copper sulfate and the sample was subjected to cathode polarization. Numerous bright deposits of copper appeared on the cathode areas, which did not coincide with the anode areas. In general the current density of the cathode areas was lower near the anode areas, but there were fewer anode areas over-all. Similar results

were obtained with the cathode indicator on aluminum, but no anode indicator has been found. The presence of all three kinds of areas previously assumed was corroborated by these electrochemical methods.—ALL.

GAS AND CONDENSATE WELL CORROSION

Statistical Analysis of Test Containers for Condensate Well Corrosion Studies. V. V. KENDALL, National Tube Co., Corrosion **3,** No. 8, 359 (1947) June.

The NACE project investigating corrosion of high pressure gas condensate wells involves insertion for 90 days into the well flow-lines of containers holding numerous standard test pieces of various materials. Results of preliminary tests to determine the number of replicates that should be used of each material, and the variability due to the type of test specimen, are reported for a 10 foot container holding 129 washer-type specimens and a 6 foot container holding 30 cylindrical specimens.

GENERAL CORROSION

Corrosion, Fouling and Methods of Maintenance of Immersed Hulls. H. MASSEILLE, Peintures, pigments, vernis, **21,** 290-291 (1945); **22,** 15-17, 290-293 (1946); Chem. Abs., **41,** No. 8, 2379 (1947) April 20.

In the corrosion of metallic hulls immersed in sea water, corrosion is not equal on the 2 sides of a hull, but the side exposed to light and the waterline are most corroded. Rivets, angular or outstanding points, and the areas near the propellers and the rudder corrode most. Protective paints of glyceride oils are rapidly saponified and penetrated by the sea water. Zinc and lead pigments have a delaying effect. A Pb_3O_4 paint is considered best. Bituminous paints are extensively used on smaller boats, but because of "bleeding" they do not tolerate an antifouling coat. Fouling was not observed on the old copper-plated wooden hulls.—INCO.

Species of Sulphur Bacteria Associated with the Corrosion of Concrete. C. D. PARKER, Nature, **159,** 439-440 (1947) Mar. 29.

Describes the isolation of certain bacteria from the corrosion products of concrete exposed to atmospheres containing hydrogen sulfide.—BLR.

METAL FAILURE

Discussion of Article on Stress-Corrosion Cracking. GEORGE F. COMWaber and McDonald and published in April Welding J. Comstock finds it difficult to accept the theory that nitrogen in steel is the cause of strain aging, caustic embrittlement and stress-corrosion cracking. He explains his objections. Author's reply is included.—BLR.

Metallographic Etchant to Reveal Temper Brittleness in Steel. J. B. COHEN, A. HURLICH AND M. JACOBSON. ASM Preprint 17, 30 pp. (1946).

Discusses metallographic etchants and procedures which are capable of differentiating between the tough and temper-brittle conditions of steels susceptible to temper embrittlement. Steels which have been embrittled either by slowly cooling from elevated tempering temperatures or during tempering at intermediate

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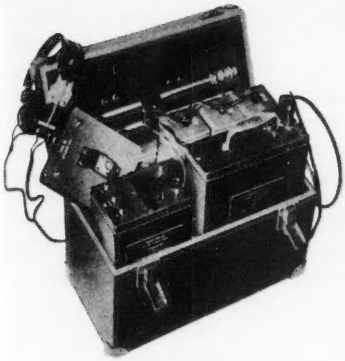
tempering temperatures show a pronounced grain boundary attack when etched in specially developed reagents. In the tough condition same steels exhibit no grain boundary attack. Steels not susceptible to temper brittleness suffer no grain boundary attack regardless of tempering cycle. Etchant can be used to determine prior austenitic grain size of alloy steels which can be temper embrittled.—BLR.

Steel Corrosion of Manganese Bronze Castings in Submarine Service. T. L. SHEEHAN AND H. E. DICKERMAN. J. Am. Soc. of Naval Engrs., **58,** No. 4, 586-598 (1946) Nov.

Manganese bronze castings conforming to Navy Department Specification 49B3e or 3F may be alloyed with a combination of elements to produce either an alpha beta or complete beta microstructure. Both types of bronze will fail by stress corrosion in sea water but the alpha beta type is less sensitive to these conditions than the complete beta bronze. The maximum average loads in excess of their yield strengths withstood were 1594 psi for beta bronze and 8625 psi for alpha beta bronze. The maximum average elongations for alpha beta bronze and beta bronze tested under stress corrosion conditions were 1.9 percent and 8.4 percent, respectively. The average immersion periods under stress corrosion conditions were 4.31 days for beta bronzes and 83.25 days for alpha beta bronzes. The failures of the beta bronze occur around grain boundaries while the failures in the alpha beta bronzes are transcrystalline. Corrosion data from sea water immersion tests and microstructure are shown.—INCO.



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Shot Peening and Its Importance in the Spring Industry. L. J. WIESCHHAUS, Wire & Wire Prod., **21,** 665-667 (1946) Sept.

Shot peening (i.e., blasting with metallic shot) is found to increase the fatigue strength of metals. Work on this subject has previously been reported, (see e.g.), H. F. Moore, "Shot Peening and the Fatigue of Metals," noted in BNF Bulletin 189, 70, (1945) Mar., and Bulletin 195, 221, (1945) Sept. The present paper deals with methods and apparatus for the peening operation.—BNF.

Fundamentals of Annealing Low Carbon Steel. G. SACHS, L. J. EBERT, B. G. KASIK and J. F. NEJEDLIK. Case School of Applied Science Iron & Steel Engr., **23,** No. 11, 88-98 (1946) Nov.

Results of investigations at the Case School to obtain a sufficiently complete picture of factors determining the properties of annealed, low-carbon steel strip are reported. Factors include: effect of cold work, annealing time and temperature, basic hardening effects, cooling rate. Among materials included were SAE 1035, low-carbon steel wire and strip and rimmed low-carbon steel. Many graphs, including: effect of cooling rate on tensile strength and lower yield point, on elongation and superficial hardness, on mechanical properties; effect of reheating and water quenching on properties of process—annealed rimmed steel; magnitude of aging effect, solid solution and hardenability effects, as shown in plotting annealing temperature against

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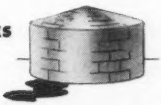

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stress. Portion of iron-carbon equilibrium diagram showing constituents present in low-carbon steel at various temperatures is presented. Effect of degrees of cold working and annealing temperature on hardness and of amount cold-rolling on recrystallization temperature of commercial pure ion reduced 5-90% in thickness are also graphed. 7 references.—INCO.

Corrosion of Buried Pipes. R. P. LINSTEAD, Queen Mary College.. Gas World, **126,** 393 (1947) Mar. 29.

In the corrosion process, oxygen ordinarily acts as the depolarizer to remove hydrogen which would slow up the reaction. In the absence of oxygen, sulphate-reducing bacteria can also serve as a depolarizer. Where conditions are favorable for the growth of these bacteria, drastic corrosion can occur in the localized form of pitting. Organic carbon is not essential for growth, as the organism will develop with carbonate as the sole carbon source. Moreover, although the vibrio develops best in the absence of oxygen, it can live in its presence. Iron is an essential growth factor. The mechanism of the action is discussed.—CEC.

Use of Alloys for Imparting Corrosion Resistance to Iron and Steel. E. A. TICE, Steel Processing, **33,** 211-215 (1947) Apr.

Discusses effects of following elements: copper; phosphorus; silicon; nickel; chromium; molybdenum; columbium and titanium; proprietary low alloy-high strength steels; and sea water, natural water, and soil corrosion.

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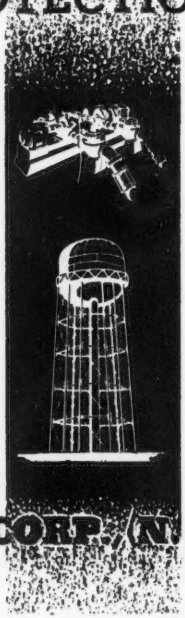

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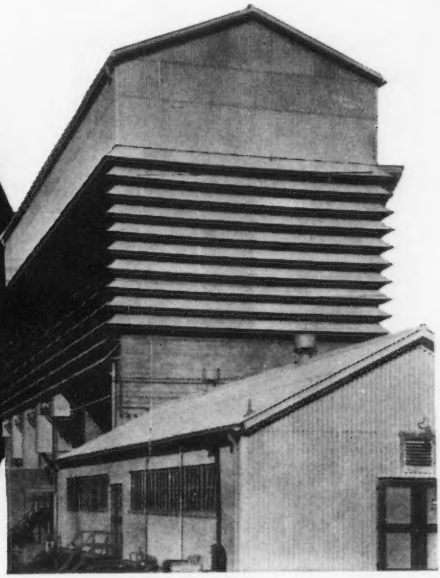

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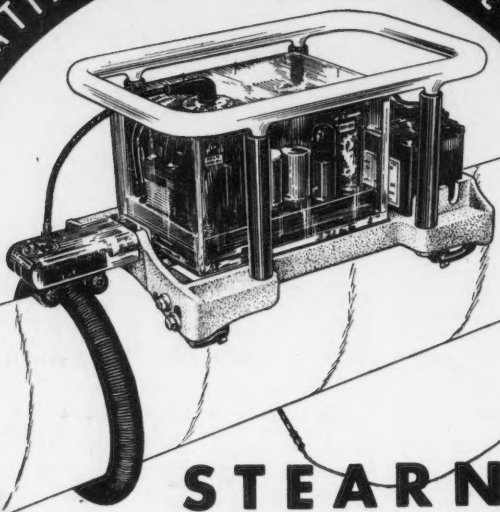

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